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Oxidation
Potentials

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THE OXIDATION STATES OF THE ELEMENTS AND THEIR POTENTIALS IN AQUEOUS SOLUTIONS, *by* Wendell M. Latimer PH.D.

The Oxidation States of the Elements *and their* Potentials in Aqueous Solutions

BY

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Preface

The most convenient method of ascertaining the relative heights of two mountains is generally by reference to a table of measured altitudes. In order to use the table, it is not necessary to understand the principles of triangulation by which the altitudes have been determined. So, also, a table of the energies of the elements in their various oxidation states may be used by one with a very elementary knowledge of thermodynamics to answer many of the qualitative questions involved in the interpretation of inorganic chemistry.

In making this summary of existing data, the author has adopted the point of view of one interested in the chemistry of the various elements, rather than the point of view of one whose interest is largely in thermodynamics as a science. The author hopes that readers of the latter class, who are disappointed at the frequent inclusion of approximate data, will find in these obvious shortcomings an incentive for careful investigations in the near future. Much of the older work should have been recalculated by modern methods, but the labor involved is beyond the capacity of a single author.

The free energies of the oxidation-reduction couples, taken with reference to the hydrogen couple, have been expressed as volts per equivalent, since this affords the simplest comparison of the relative driving power of the various couples. However, for completed oxidation-reduction reactions, the free energies have been given in calories, as the number of equivalents of electricity is sometimes ambiguous. Solubility products and the dissociation constants of weak acids, bases, and complex ions have been included whenever the data were available.

The author, in calculating many new free energies from reaction heats, has drawn largely upon his own experimental work on the entropies of solids and aqueous ions. Our present knowledge of the entropy values permits the estimation of many entropies from the values of similar substances, and these estimates have frequently been employed in third-law calculations to obtain approximate reaction potentials.

Potentials have been given for many couples which are not thermodynamically reversible. These values, of course, cannot be used in equilibrium reasoning. However, these potentials are of value in indicating the minimum energy which must be employed to accomplish the oxidation or reduction, and they often give considerable information regarding the possible reaction mechanisms and the cause of the slowness of the reactions.

In some cases it would be valuable to list potentials for couples at 1 M concentration, rather than list the E° values. However, these molal potentials are not so useful as one might at first think. They can be used accurately only at 1 M concentration; and, if an approximate value is desired, the E° without corrections for the activity might as well be used.

References have been given for all values employed. These references may usually be consulted for additional references to older works. The author has endeavored to include in his references all works published up to 1938.

Some mention should be made of the author's attempt to avoid the confusion existing with regard to the use of the term *valence*. This term has been restricted to mean, in the organic chemistry sense, the number of bonds (electron pairs) which an atom shares with other atoms. Such a usage renders the terms *covalence* and *coördination number* unnecessary but requires additional nomenclature to designate the charge upon an atom. In many cases this charge is a readily determinable number as, for example, the charge of -1 on chloride ion. This charge will be called the *polar number*. In a large number of compounds the polar number of each atom cannot be readily determined experimentally, but a fair approximation is obtained by assuming that the two electrons of a bond are shared equally between the two atoms. On this basis the charge upon the sulfur atom in sulfate is $+2$ and that upon each oxygen is -1. The term *formal polar number* has been suggested for the charge estimated in this manner.

However, for the purpose of classification, a still more arbitrary method of assigning values to the charges upon the atoms of a compound has proved extremely useful. As an example, we may again use the sulfate ion. This method assumes that each oxygen has a charge of -2, which then gives a charge of $+6$ to the sulfur. These assumptions not only simplify the classification of compounds but are also valuable in the interpretation of oxidation-reduction reactions. Thus, the +6 charge on the sulfur may be correlated with the six electrons involved in the half-reaction for the oxidation of sulfur to sulfate,

$$S + 4H_2O = 8H^+ + SO_4^{--} + 6e^-.$$

Similar half-reactions may be written for the oxidation (or reduction) of any free element to any of its compounds, and the number of electrons involved in the reaction may be used to define the oxidation number or oxidation state of the element.

To summarize the illustration of nomenclature for the sulfate example, we may state: the valence of the sulfur is four; the polar number is unknown, but the formal polar number is +2; and the oxidation state is +6.

The author owes much to the spirit of coöperation which has been so carefully fostered in this department by Professor Gilbert N. Lewis. In the author's opinion there is no man who has such a complete understanding of the mechanism of inorganic reactions as does Professor William C. Bray, and he is especially indebted to Professor Bray for the advice so willingly given on many problems. The author wishes to thank both the many graduate students who have read and criticized the manuscript and Dr. George G. Manov for his recalculation of many of the free energies.

WENDELL M. LATIMER

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Oxidation
Potentials

CHAPTER I

Units, Conventions, and General Methods Employed in the Determination of Oxidation-Reduction Potentials

As stated in the Preface, the primary object of this work is to gather together the large mass of free-energy data which is scattered throughout the literature and to present it in a simple form as an aid in the interpretation of inorganic chemistry. Although the author does not wish to stress in detail the methods by which these data have been obtained, it seems desirable, for the sake of clarity, to discuss in a preliminary chapter general methods and to give references to more detailed treatments.

The potentials have been derived from four sources: (1) the direct measurement of cells, (2) equilibrium data, (3) thermal data, and (4) approximate limiting values based upon the chemical behavior of a couple with respect to known oxidizing and reducing agents. Before outlining these methods, a statement of the energy units employed and the general conventions in nomenclature will be given.

Energy units. The unit of potential employed is the international volt. This is related to the absolute volt by the equation,

1 volt (international) = 1.0004 volts (absolute).

The international joule, defined by the international units for the volt, ampere, and ohm, is the unit of energy. When it is desired to express energies in calories, the defined calorie used by Bichowsky and Rossini[1] has been employed.

1 calorie (defined) = 4.1833 joules.

Other units which enter into various calculations are:

0° Centigrade = 273.15° Absolute or Kelvin,

1 Faraday = 1 equivalent = 96,494 coulombs (international),

1 volt equivalent = 23,066 calories (defined),

R (gas constant) = 8.3118 joules (international) per degree per mole.

---

[1] Bichowsky, F. R., and Rossini, F. D., *Thermochemistry of the Chemical Substances* (Reinhold, New York, 1936), p. 9.

Temperature. Unless otherwise stated, all potentials are given for the temperature of 25° C. or 298.15° K. The choice of the best value for 0° C. on the absolute scale is difficult. The value 273.1 is certainly too low. It is to be hoped that some definite agreement on the value to be used will be reached in the near future.

$E°$ values. A potential is referred to as an $E°$ value if all gases involved in the reaction are at a fugacity (thermodynamic pressure) of 1 atmosphere and all dissolved substances at an activity (thermodynamic concentration) of 1 molal, *i.e.*, 1 mole per 1000 grams of water.

The potential, E, at other concentration and pressures at 25° C. is given by the expression:

$$E = E° - \frac{0.05914}{n} \log_{10} Q, \tag{1}$$

where Q is the product of the activities (or fugacities) of the resulting substances divided by the product of the activities of the reacting substances, each activity raised to that power whose exponent is the coefficient of the substance in the chemical equation; and n is the number of Faradays of electricity involved in the reaction as written. Thus Q has the same general form as the equilibrium constant, but it differs in that the activities refer not to the equilibrium state but to the actual activities of the reacting substances and their products. Activities of pure solids and liquids are taken as unity. For the equilibrium state, Q becomes the equilibrium constant, K, and since E for a reaction at equilibrium is zero,

$$E° = \frac{0.05914}{n} \log K. \tag{2}$$

Hydrogen reference couple. Any oxidation-reduction reaction may be broken up into two "half-reactions" or "couples" that indicate the mechanism by which the electrons are transferred from the reducing agent to the oxidizing agent. For example, in the reaction,

$$2Ag^+ + H_2 = 2Ag + 2H^+,$$

the two half-reactions, or couples, are:

$$Ag = Ag^+ + e^-, \text{ and}$$

$$H_2 = 2H^+ + 2e^-.$$

The experimental determination of the absolute potential of any couple is a different problem (cf. p. 21), but since any chemical reaction involves only the difference in potential between two couples, the absolute values are unnecessary. For this reason the procedure has come into general use of choosing the potential of some one couple as an arbitrary zero and using this as a reference couple for potentials of all other couples. The reference couple so chosen is the hydrogen gas-hydrogen ion couple:

$$H_2 = 2H^+ + 2e^-, \qquad E° = 0$$

Reactions which involve hydroxide ion will also be referred to the hydrogen couple, but in such solutions this couple has the form (cf. p. 28),

$$H_2 + 2OH^- = 2H_2O + 2e^-, \qquad E° = 0.828$$

The $E°$ values of half-reactions in alkaline solution will be designated as $E°_B$ to indicate that this basic potential of the hydrogen couple must be used to obtain the completed reaction potential against hydrogen.

EXAMPLE

$$Cl^- + 2OH^- = ClO^- + H_2O + 2e^-, \qquad E°_B = -0.94$$

$$ClO^- + H_2 = Cl^- + H_2O, \qquad E° = 0.83 + 0.94 = 1.77$$

Conventions regarding sign. All couples will be written with the electrons on the right hand side of the equation. A positive value for $E°$ will mean that the reduced form of the couple is a better reducing agent than H_2. For example,

$$Zn = Zn^{++} + 2e^-, \qquad E° = 0.762$$

will mean that the reaction,

$$Zn + 2H^+ = Zn^{++} + H_2,$$

goes as written with a potential of 0.762 volts. And similarly a negative $E°$ will mean that the oxidized form of the couple is a better oxidizing agent than H^+. For example,

$$Cu = Cu^{++} + 2e^- \qquad E° = -0.345$$

will mean that the reaction,

$$Cu^{++} + H_2 = Cu + 2H^+,$$

goes as written with a potential of 0.345 volts.

The convention, illustrated in these examples, of giving a positive sign to the potential of any complete reaction, which goes spontaneously in the direction as written, will be followed.

Addition or subtraction of half-reaction potentials. When one half-reaction is subtracted from another to give a complete reaction, the potential of the complete reaction is the algebraic difference in the potentials of the two half-reactions.

EXAMPLE

$$\begin{array}{rcl@{\qquad}rcr}
Zn & = & Zn^{++} + 2e^- & E^\circ & = & 0.762 \\
2Ag & = & 2Ag^+ + 2e^- & E^\circ & = & -0.799 \\
\hline
Zn + 2Ag^+ & = & Zn^{++} + 2Ag & E^\circ & = & 1.561
\end{array}$$

However, in the addition or subtraction of two half-reactions to give a third half-reaction, the free energies, *i.e.*, volt equivalents of the two half-reactions must be added or subtracted to give the free energies of the third half-reaction.

EXAMPLE

$$\begin{array}{rcl@{\qquad}r@{\qquad}r}
 & & & E^\circ & \textit{Volt equivalents} \\
Cl^- + 3H_2O & = & ClO_3^- + 6H^+ + 6e^- & -1.45 & -8.70 \\
Cl^- & = & \frac{1}{2}Cl_2 + e^- & -1.36 & -1.36 \\
\hline
\frac{1}{2}Cl_2 + 3H_2O & = & ClO_3^- + 6H^+ + 5e^- & -1.47 & -7.34
\end{array}$$

Potentials from Galvanic Cells

Cells without liquid junctions. The potential of a fairly large number of reactions may be measured directly in cells having a single electrolyte. Thus, for the reaction

$$2AgCl + H_2 = 2Ag + 2H^+ + 2Cl^-$$

having as half-reactions,

$$H_2 = 2H^+ + 2e^- \text{ and}$$

$$AgCl + e^- = Ag + Cl^-,$$

a cell may be constructed, using as one electrode metallic silver in contact with silver chloride, and as the other electrode hydrogen gas in contact with hydrogen ion on a platinum surface. The electrolyte throughout the cell may then be hydrochloric acid and is uniform except for the slight solubility of silver chloride. The two electrode reactions must be reversible and reasonably rapid. On many surfaces the hydrogen couple does not meet this requirement, but the reaction is sufficiently catalyzed by a platinized platinum surface. In the construction of any cell, the reducing and oxidizing agents must not come into direct contact with each other. Moreover the reducing agent must be the strongest reducing agent present at the anode and the oxidizing agent must be the strongest oxidizing agent present at the cathode. These requirements are met by the above cell with the exception that, if air is not excluded, the oxygen is a stronger oxidizing agent than silver chloride. However, its action is slow under these conditions and its exclusion from the cathode is therefore not necessary in this case.

From the electromotive force of this cell at any given concentration of hydrochloric acid and pressure of hydrogen, the E° value may be calculated from equation (1), if the activities of the hydrogen and chloride ions are known. Strictly speaking, it is not possible to measure the activity of an ion of one sign independently of the ion of opposite sign, so the information required is the *mean activity*, $a\pm$, of the two ions. By definition, the *activity coefficient*, γ, is the ratio of the mean activity to the mean molality, $m\pm$. That is,.

$$\gamma = \frac{a\pm}{m\pm}. \tag{3}$$

At infinite dilution, the activity equals the molality and γ equals 1; and for each type of salt, the mean molality is defined in such a way that the ratio approaches unity at infinite dilution (cf. Appendix IV). If the potential measurements are carried out in dilute solutions, one may assume the concentration equal to the activity and calculate approximate E° values. However for the highest accuracy it is necessary to determine the γ values, and Appendix IV should be consulted for general references dealing with these experimental procedures. Fairly complete values of γ for various types of salts are also given in this appendix, and the following example illustrates their use in calculating E° values.

The measured potential of a silver, silver chloride-hydrogen ion, hydrogen cell at a hydrogen pressure of 0.962 atmospheres and a molality of 0.100 for the hydrochloric acid is 0.3516 volts. The γ for the molality of this acid is 0.796. Assuming the hydrogen to be a sufficiently perfect gas so that no correction need be made for deviations from the gas laws, one may then write the reactions,

$$AgCl + \tfrac{1}{2}H_2 = Ag + Cl^- + H^+$$

$$0.3516 = E^\circ - \frac{0.05914}{n} \log_{10} \frac{a_{H^+}a_{Cl^-}}{(P_{H_2})^{\frac{1}{2}}}$$

$$= E^\circ - 0.05914 \log_{10} \frac{(0.796 \times 0.1)^2}{(0.962)^{\frac{1}{2}}}.$$

$$E^\circ = 0.2221 \text{ for the reaction and}$$

$$Cl^- + Ag = AgCl + e^-, \qquad E^\circ = -0.2221$$

The activity coefficient may be thought of as the thermodynamic ionization constant, but the modern theory of strong electrolytes assumes that they are completely ionized, in the sense that the ions are capable of independent motion and that the apparent nonionization results from the forces acting between an ion and its neighbors in general rather than its attraction to any particular ion. The Debye and Hückel[2] theory has been very successful in calculating activity coefficients from the electrostatic forces in very dilute solutions. At high concentrations other factors enter, such as the force of repulsion between the large hydrated ions or the change in the hydration of the ions, and the activity coefficient often becomes greater than unity or the apparent ionization greater than 100 per cent. The theoretical treatment of the concentrated solutions is still incomplete. Appendix IV should also be consulted for a discussion of the principle of ionic strength.

Cells with liquid junctions. Many cells may be constructed which have one electrolyte around the cathode and another around the anode. The familiar zinc-copper gravity cell is an example, the anode consisting of zinc in a solution of zinc sulfate and the cathode of copper in a copper sulfate solution. The accurate evaluation of the E° potentials for such cells involves the same general problem of the activity coefficients discussed in the previous section, together with the added difficulty of determining the potential which exists at the junction of the two electrolytes. For the simple case of salts of monovalent positive and negative ions, good theoretical evaluations of the liquid junction potential may be made,[3] but with many electrolytes the problem is a difficult one.[4] A bridge of concentrated potassium chloride often reduces the liquid potential to a few millivolts.

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[2] Debye, P., and Hückel, E., Phys. Z., **24**, 185, 305 (1923). Cf. also the review by La Mer, V. K., Trans. Am. Electrochem. Soc., **51**, 507 (1927).

Potential Values from Free Energies and Equilibrium Constants

The free energy ΔF of a chemical reaction is the maximum available work which can be obtained in going from the initial to the final state, and is related to the reaction potential by the equations:

$$\Delta F(\text{joule}) = -E \cdot n \cdot 96{,}494 \qquad \textbf{(4a)}$$

$$\Delta F(\text{cal.}) = -E \cdot n \cdot 23{,}066 \qquad \textbf{(4b)}$$

The symbol ΔF° is used when all the reacting substances are at unit activity. The free energy of formation of a substance (often called simply the free energy of the substance) refers to its formation from its elements, and the free energies of all elements and H^+ are taken as zero in their standard states of unit activity.

EXAMPLE

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}N_2 + \tfrac{3}{2}O_2 = H^+ + NO_3^- \qquad \Delta F^\circ = -26{,}250 \text{ cal.}$$

$$\Delta F^\circ \text{ of formation of } NO_3^- = F^\circ_{NO_3^-} = -26{,}250 \text{ cal.}$$

The free energy of a reaction is the sum of the free energies of formation of the products of the reaction, less the sum of the free energies of formation of the reacting substances.

EXAMPLE

$$3I^- + H_2O_2 + 2H^+ = I_3^- + 2H_2O$$

$$\begin{aligned} \Delta F^\circ &= F^\circ_{I_3^-} + 2F^\circ_{H_2O} - 3F^\circ_{I^-} - F^\circ_{H_2O_2} - 2F^\circ_{H^+} \\ &= (-12{,}290) + 2(-56{,}690) - 3(-12{,}333) \\ &\quad - (-31{,}470) - 2(0) \\ &= -57{,}201 \text{ cal.} \end{aligned}$$

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[3] MacInnes, D. A., International Critical Tables, VI, 338.

[4] Lewis, G. N., and Randall, M., *Thermodynamics and the Free Energy of Chemical Substances* (McGraw-Hill, New York, 1923), p. 333.

The E° for the reaction may then be calculated from equation (4b).

$$E^\circ = \frac{57{,}201}{2 \times 23{,}066} = 1.239 \text{ volts}$$

The relation between the free energy of a chemical reaction and the equilibrium constant is:

$$\Delta F = -RT \ln \frac{K}{Q}, \tag{5}$$

where R is the gas constant, T the absolute reaction temperature, K the equilibrium constant, and Q a constant which has the same form as K but in which the concentrations refer to the actual values for the substances in the reaction. When all substances are at unit concentration, $Q = 1$ and $\Delta F = \Delta F^\circ$.

$$\Delta F^\circ = -RT \ln K \tag{6a}$$

$$\Delta F^\circ_{298.15}(\text{cal.}) = -1364.0 \log_{10} K \tag{6b}$$

A knowledge of the equilibrium constant thus permits the calculation of ΔF° and E°.

EXAMPLE

For the reaction,

$$2Cl_2 + 2H_2O = O_2 + 4Cl^- + 4H^+,$$

the equilibrium constant has been determined at 25° C. as 1.122×10^9. Hence,

$$\Delta F^\circ = -1364.0 \log_{10} K = -12{,}344 \text{ cal.}$$

$$E^\circ = \frac{12{,}348}{4 \times 23{,}066} = 0.134 \text{ volts.}$$

Potential Values from Thermal Data

When zinc dissolves in hydrochloric acid, or to make the conditions more exact, in hydrochloric acid containing some definite concentration of zinc ion, the chemical energy, with the exception of the small amount of work which is done against the atmospheric pressure, is converted into heat. This heat is called the heat of the reaction or the change in heat content, ΔH, and differs from the free energy or the reversible energy by a quantity called the "irreversible energy," which is equal to the absolute temperature times the entropy of the reaction, ΔS.

$$\Delta F = \Delta H - T\Delta S \tag{7}$$

ΔF° and E° may then be calculated if the corresponding ΔH° and ΔS° values are known.

Reference should be made to standard works on thermal chemistry[5] for the general calorimetric methods employed in the experimental determination of ΔH°. For the calculations in this book the author has used very largely the values summarized by Bichowsky and Rossini.[6] They have chosen 18° C. as their basic temperature. In many cases the correction to 25° C. is less than the experimental error in ΔH, but when accurate specific heat data are available the corrections have been made.

The entropy, S°, of a pure solid at 298.15° C. is given by the equation,

$$S^\circ = \int_0^{298.15} C_p d \ln T + R \ln g, \tag{8}$$

where C_p is the specific heat at constant pressure and g the number of detailed states or the multiplicity of the solid when cooled to absolute zero. For all substances, C_p becomes zero at very low temperatures and if the substance in its lowest energy level has but a single configuration, g then equals unity and *the entropy of the substance at the absolute zero is zero.*

The italicized clause is a statement of the Third Law of Thermodynamics. The validity of this law, which has been the subject of much controversy during the past two decades, can no longer be doubted. Its application has made possible the experimental evaluation of absolute entropies from specific heat measurements and thus the calculation of ΔF° and E° from thermal data by equation (7). At least half of the free energies which we shall employ have been computed by this method.

Figure 1 gives a typical plot of C_p against log T. The area under the curve is a graphical integration of the integral in equation (8), and hence the entropy of barium sulfate at 298° K.

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[5] Thomsen, J., *Thermochemische Untersuchungen* (Barth, Leipzig, 1886). Rossini, F. D., U. S. Bur. Standards Research Paper 686 (1934).

[6] Bichowsky, F. R., and Rossini, F. D., *Thermochemistry* (Reinhold, New York, 1936).

It is obvious from equation (8) that caution must be observed in applying the third law to substances which may have multiplicity in this lowest energy state. Investigations of large numbers of substances have now indicated fairly well the types of compounds in which this may be true.

To obtain the entropy of a substance which is liquid at 25° C., it is necessary to determine the entropy of the solid at the melting point, the entropy of fusion (heat of fusion/absolute temperature) and the C_p– log T curve for the liquid. Similarly, for a gas, the additional information needed is the entropy of vaporization and the C_p—log T curve for the gas.

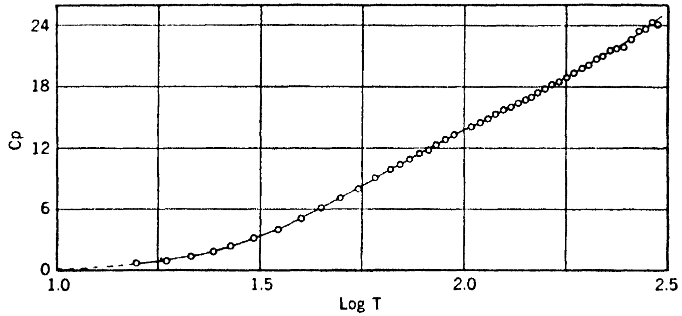

FIG. 1.—Molal heat capacity of $BaSO_4$ against log of absolute temperature.

For a number of comparatively simple gas molecules, spectroscopy has supplied complete information in regard to the number of quantum states and their energies. By purely statistical methods the entropy of such gases may be calculated from these data.[7] The spectroscopic entropies have been a very valuable check on the corresponding values calculated from specific heat data[8] and have served to show the types of molecules which have multiplicity at absolute zero, or rather, the molecules in which transitions to the lowest state do not occur in the temperature range used for specific heat measurements.

Extensive use has been made of the entropies of the aqueous ions which have been determined by the author and his co-workers.[9]

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[7] Giauque, W. F., J. Am. Chem. Soc., **52**, 4808 (1930).

[8] Eastman, E. D., Chem. Rev., **18**, 257 (1936).

[9] Latimer, W. M., Schutz, P. W., and Hicks, J. F. G., Jr., J. Chem. Phys., **2**, 82 (1934). Latimer, W. M., Chem. Rev., **18**, 349 (1936). Latimer, W. M., Smith, W. V., and Pitzer, K. S., J. Am. Chem. Soc., **60**, 1829 (1938).

These entropies have been obtained from the entropies of compounds at 25° C. and their entropies of solution as calculated from the heats and free energies of solution by equation (7). The heats of formation are known for many substances in solution for which it has been impossible to determine the free energies by electromotive force or equilibrium methods because of the slowness or irreversibility of the reactions. A knowledge of the entropy values has thus made available these thermal data for the calculation of reaction potentials. For the most reliable data, the accuracy obtained is of the order of 0.001 to 0.01 volts. In some cases, however, the errors in the heats of reaction may run as high as 2000 calories per equivalent which would give errors of 0.1 in the potentials. The various experimental entropy values are summarized in Appendix V. The entropy of a substance which has not been determined experimentally may be closely estimated from the values of a similar substance, and in many cases such values have been used.

The following example will serve to illustrate the use of thermal data in potential calculations.

EXAMPLE

$$\tfrac{1}{2}H_2 + AgCl(s) = H^+ + Cl^- + Ag(s)$$

$$\Delta H^\circ = -9600 \text{ cal.}$$

$$\Delta S^\circ = S^\circ_{H^+} + S^\circ_{Cl^-} + S^\circ_{Ag} - \tfrac{1}{2}S^\circ_{H_2} - S^\circ_{AgCl}$$

$$= 0 + 13.5 + 10.2 - \tfrac{1}{2} \times 31.2 - 23.0 = -14.9$$

$$\Delta F^\circ = -9600 - 298.15 \times (-14.9) = -5155 \text{ cal.}$$

$$E^\circ = \frac{-5155}{23{,}066} = 0.223 \text{ volts.}$$

Hence,

$$Ag(s) + Cl^- = AgCl + e^-, \qquad E^\circ = -0.223 \text{ volts.}$$

Estimation of Potential Values from Chemical Evidence

For the interpretation of inorganic chemistry, the knowledge of the approximate value, say within 0.2 volts, of an oxidation-reduction couple is often as valuable as a potential given to a thousandth of a volt. There are many reactions for which every type of thermodynamic data is lacking but for which there is sufficient chemical data, in the form of reactions with oxidation-reduction couples of known potentials, to fix the value within narrow limits.

A single example will serve to illustrate the method. Samarous ion, Sm^{++}, reduces water readily, and the sulfate $SmSO_4$ acts slowly. Since the size of samarous ion is about that of barium ion, the solubilities of the sulfate should be about that of barium sulfate, roughly 10^{-5} moles per liter. Hence the couple,

$$Sm^{++}(10^{-5}M) = Sm^{+++} + e^-,$$

is more positive than the couple,

$$\tfrac{1}{2}H_2 = H^+(10^{-7}M) + e^-, \qquad E = 0.414$$

Correcting for the low concentration of Sm^{++}, we obtain

$$\Delta E = -0.059 \log \frac{1}{Sm^{++}} = 0.059 \times 5 = 0.30.$$

One can then say that the samarium couple is somewhat more positive than 0.71, probably about 0.8.

$$Sm^{++} = Sm^{+++} + e^-, \qquad E^\circ = \text{ca } 0.8$$

CHAPTER II

Ionization Potentials, Electron Affinities, Lattice Energies, and their Relation to Standard Oxidation-Reduction Potentials

The values for the ionization potentials and the electron affinities of the elements have contributed much to the interpretation of many types of chemical reactions, and it is important to consider the relation of these quantities, obtained for the monatomic gas atoms, to the oxidation-reduction potentials of the elements and their compounds in their standard states at 25° C. It is also interesting to see to what extent the atomic energies can be used to answer such questions as why silver is a noble metal and sodium basic or why fluorine is more electronegative than iodine.

Ionization potentials. The analysis of atomic line spectra has provided highly accurate values for the ionization potentials. For most atoms the potential required to remove one or all of the valence electrons is known, and it is known in some cases for electrons from the closed shell lying below the valence electrons. A summary of these potentials is given in Table 1[1] (see p. 14).

Some interesting relations may be observed in the first ionization potential of the various atoms. The value depends upon the type of electron, *s*, *p*, *d*, or *f*; upon the total quantum number; and upon the number of electrons already in the uncompleted shell. It will be seen that maximum potentials are attained for the noble gases, with the completion of the 1*s* shell for helium and of the eight electrons of the *s* and *p* groups for the other gases; and the minimum potentials occur in the alkali metals which have but a single *s* electron in the valence shell. The first *p* electron has a slightly lower value than the preceding *s* electron, and the potentials for succeeding *p* electrons rise rapidly, with the exception of a slightly lower value for the fourth *p* electron. For the process of filling up the *d* and *f* groups, the potentials are

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[1] Herzberg, G., *Atomic Spectra and Atomic Structure* (Prentice-Hall, New York, 1937), pp. 200-201.

TABLE 1
IONIZATION POTENTIALS OF THE ELEMENTS

(Values are expressed in volts. Uncertain values are indicated by ∼.)

Element	I	II	III	IV	V
1 H	13.527	—	—	—	—
2 He	24.46	54.14	—	—	—
3 Li	5.363	75.26	121.8	—	—
4 Be	9.28	18.12	153.1	216.6	—
5 B	8.257	25.00	37.75	258.1	338.5
6 C	11.217	24.27	47.65	64.22	390.1
7 N	14.48	29.47	47.40	77	97.43
8 O	13.550	34.93	54.87	76.99	113
9 F	17.34	34.81	62.35	86.72	113.67
10 Ne	21.45	40.9	63.2	—	—
11 Na	5.12	47.06	70.72	—	—
12 Mg	7.61	14.96	79.72	108.9	—
13 Al	5.96	18.74	28.31	119.37	153.4
14 Si	8.12	16.27	33.35	44.89	165.6
15 P	10.9	19.56	30.0	—	64.70
16 S	10.30	23.3	34.9	47.08	63
17 Cl	12.952	23.67	39.69	53.16	67.4
18 A	15.68	27.76	40.75	∼61	∼78
19 K	4.318	31.66	46.5	—	—
20 Ca	6.09	11.82	50.96	69.7	—
21 Sc	∼6.7	∼12.8	24.61	∼73.9	97.0
22 Ti	6.81	∼13.6	∼27.6	42.98	∼99.6
23 V	6.71	14.1	∼26.4	∼48	∼65
24 Cr	6.74	∼16.6	—	—	∼73
25 Mn	7.41	15.70	—	—	∼76
26 Fe	7.83	16.16	—	—	—
27 Co	7.81	17.3	—	—	—
28 Ni	7.61	18.2	—	—	—
29 Cu	7.68	20.2	—	—	—
30 Zn	9.36	17.89	40.0	—	—
31 Ga	5.97	20.43	∼30.6	63.8	—
32 Ge	8.09	15.86	34.07	45.5	93.0
33 As	10.5	20.1	28.0	49.9	62.5
34 Se	9.70	21.3	33.9	42.72	72.8
35 Br	11.80	19.1	25.7	—	—
36 Kr	13.93	∼26.4	36.8	∼68	—

TABLE 1 (*Continued*)

IONIZATION POTENTIALS OF THE ELEMENTS

(Values are expressed in volts. Uncertain values are indicated by ~.)

Element	I	II	III	IV	V
37 Rb	4.159	27.36	~47	~80	—
38 Sr	5.667	10.98	—	—	—
39 Y	~6.5	12.3	20.4	—	—
40 Zr	6.92	13.97	24.00	33.8	—
41 Cb	—	—	24.2	—	49.3
42 Mo	7.35	—	—	—	60.8
45 Rh	7.7	—	—	—	—
46 Pd	8.3	19.8	—	—	—
47 Ag	7.54	21.4	35.9	—	—
48 Cd	8.96	16.84	38.0	—	—
49 In	5.76	18.79	27.9	57.8	—
50 Sn	7.30	~14.5	30.5	39.4	80.7
51 Sb	—	~18	24.7	44.0	55.5
52 Te	8.96	—	30.5	37.7	60.0
53 I	10.6	19.4	—	—	—
54 Xe	12.08	~21.1	32.0	~46	~76
55 Cs	3.87	23.4	~35	~51	~58
56 Ba	5.19	9.95	—	—	—
57 La	5.6	11.4	~20.4	—	—
58 Ce	6.54	14.8	—	~36.5	—
62 Sm	—	11.4	—	—	—
63 Eu	5.64	11.4	—	—	—
76 Os	~8.7	—	—	—	—
78 Pt	8.88	—	—	—	—
79 Au	9.18	19.95	—	—	—
80 Hg	10.38	18.65	34.3	~72	~82
81 Tl	6.07	20.32	29.7	50.5	—
82 Pb	7.38	14.96	~31.9	42.11	69.4
83 Bi	—	16.6	25.42	45.1	55.7
86 Rn	10.698	—	—	—	—
88 Ra	5.252	10.099	—	—	—
90 Th	—	—	29.4	—	—

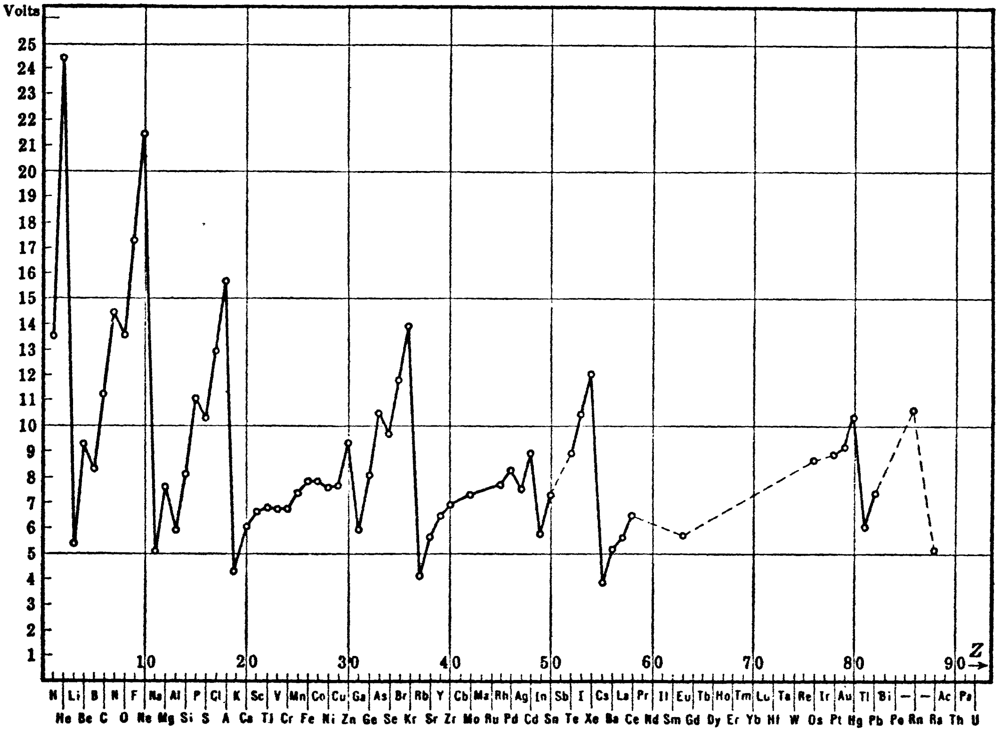

FIG. 2.—Dependence of the ionization potentials of the neutral atom on atomic structure.

fairly constant, with just a slight but often irregular rise as the number of electrons in the group increases. The relations are shown graphically in Figure 2, which is taken from Herzberg.[2]

Electron affinities. The evaluation of the electron affinities of the electronegative elements, namely, the potentials for the capture of one or more electrons by the monatomic gas atoms, has been difficult inasmuch as the methods of line spectra have not been applicable. In a few cases direct determinations have been made as, for example, iodine—by Sutton and Mayer,[3] but most of the values given in Table 2 have been obtained by indirect calculations.[4] (Cf. lattice energies below.)

TABLE 2

ELECTRON AFFINITIES

Element	Volts	Element	Volts
$H + e^- = H^-$	−0.08	$O + e^- = O^-$	2.2
$F + e^- = F^-$	4.13	$S + e^- = S^-$	2.8
$Cl + e^- = Cl^-$	3.75	$O + 2e^- = O^{--}$	−7.3
$Br + e^- = Br^-$	3.53	$S + 2e^- = S^{--}$	−3.4
$I + e^- = I^-$	3.22		

Reactions at 25° C. Unfortunately for the direct application of ionization potentials and electron affinities to the general problem of chemical-free energies, most elements and their ions do not exist at room temperatures as monatomic gases. Moreover when one attempts to use the data for the gaseous atoms to calculate reaction potentials under ordinary reaction conditions, there is usually at least one step in the process which is difficult to evaluate accurately. Two examples will be given to illustrate this difficulty.

1. The energy of the reaction between silver and iodine,

$$2Ag(s) + I_2(s) = 2AgI(s), \qquad (1)$$

could be calculated as the sum of the following steps:

SUBLIMATION ENERGY: $I_2(s) = I_2(g)$

DISSOCIATION ENERGY: $I_2(g) = 2I(g)$

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[2] *Ibid.*, p. 217.

[3] Sutton, P. P., and Mayer, J. E., J. Chem. Phys., **3**, 20 (1935).

[4] Mayer, J. E., and Helmholz, L., Z. Physik, **75**, 19 (1932); Sherman, J., Chem. Rev., **11**, 94 (1932); Pauling, L., Phys. Rev., **29**, 285 (1927). See also value for hydrogen by Hylleraas, E. A., Z. Physik., **65**, 209 (1930).

Electron affinity: $2\mathrm{I(g)} + 2e^-\mathrm{(g)} = 2\mathrm{I^-(g)}$

Sublimation energy: $2\mathrm{Ag(s)} = 2\mathrm{Ag(g)}$

Ionization energy: $2\mathrm{Ag(g)} = 2\mathrm{Ag^+(g)} + 2e^-\mathrm{(g)}$

Lattice energy: $\mathrm{Ag^+(g)} + \mathrm{I^-(g)} = \mathrm{AgI(s)}$

But the energy of the last reaction, the lattice energy (*i.e.*, the energy required to separate the ions of solid silver iodide to infinity), cannot be directly determined. However, in a few cases the lattice energies (vide infra) can be theoretically estimated and used, with a series of reactions such as the above, to calculate reaction potentials.

2. The energy of the reaction between hydrogen and chlorine to form hydrochloric acid in solution,

$$\mathrm{H_2(g)} + \mathrm{Cl_2(g)} = 2\mathrm{H^+(aq)} + 2\mathrm{Cl^-(aq)}, \qquad (2)$$

could be calculated as the sum of the following steps:

Ionization energy: $2\mathrm{H(g)} = 2\mathrm{H^+(g)} + 2e^-\mathrm{(g)}$

Dissociation energy: $\mathrm{H_2(g)} = 2\mathrm{H(g)}$

Hydration energy: $2\mathrm{H^+(g)} = 2\mathrm{H^+(aq)}$

Electron affinity: $2\mathrm{Cl(g)} + 2e^-\mathrm{(g)} = 2\mathrm{Cl^-(g)}$

Dissociation energy: $\mathrm{Cl_2(g)} = 2\mathrm{Cl(g)}$

Hydration energy: $2\mathrm{Cl^-(g)} = 2\mathrm{Cl^-(aq)}$

The two hydration energies cannot be obtained experimentally; hence the process is not a feasible method of determining the potential of the chlorine-hydrogen reaction.

However, it is obvious that, if the energies of the two reactions, (1) and (2), are known, they may be used to calculate, in the first case, the lattice energy of the silver iodide, and in the second, the sum of the hydration energies of hydrogen and chloride ions. In this way the so-called experimental values for these quantities have been obtained.

Lattice energies. When the values for these energies were first tabulated, it was evident that they were largely coulombic in nature, that is, they were roughly directly proportional to the product of the changes of the ions and inversely to the distance between the ions in the solid. Born and Landé[5] first attacked the problem of their theoretical evaluation as a purely electrostatic calculation, assuming that the ions are held in equilibrium in the lattice by attractive forces which are coulombic and repulsive forces which change rapidly with the distance. Later workers have so refined the methods that, for the alkali halides at least, the theoretical values are probably better than the experimental, since the latter depend upon somewhat questionable data for the electron affinities. In fact, the best values for the electron affinities are obtained by solving for them in series of equations such as those in example 1 and using the theoretical values for the alkali halide lattice energies. The data for Table 3 are those given by Mayer and Helmholz[6] for the alkali halides and by Sherman[7] for the other compounds. The latter reference may be consulted for additional data.

TABLE 3
LATTICE ENERGIES IN KCAL. AT 0° K.

Ion	F^-	Cl^-	Br^-	I^-	O^{--}
Li^+	240.1	199.2	188.3	174.1	693
Na^+	213.4	183.1	174.6	163.9	—
K^+	189.7	165.4	159.3	150.8	—
Rb^+	181.6	160.7	153.5	145.3	—
Cs^+	173.7	152.2	146.3	139.1	—
Ag^+	223.0	207.0	204.0	202.0	715
Cd^{++}	662.0	—	—	563.0	911

Hydration energies. Since the energies of solution of solid salts are small in comparison to the large lattice energies, it follows that the lattice energy must be approximately the same as the sum of the energies of hydration of the two ions. In other words the water dipoles neutralize the electrical fields of the ions to about the same extent that the ions neutralize each other in the crystal, unless, as is sometimes the case, the negative ion is highly polarized in the solid. Any evaluation from experimental data always gives the sum of the hydration of the negative and positive ions. A summary of the data for the ions of a number of common salts is given in Table 4.

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[5] Born, M., and Landé, A., Sitzber. königl. preuss. Akad. Wiss. Berlin, **45,** 1048 (1918).

[6] Mayer, J. E., and Helmholz, L., Z. Physik, **75,** 19 (1932).

[7] Sherman, J., Chem. Rev., **11,** 94 (1932).

TABLE 4

ENERGIES OF SOLUTION OF GASEOUS IONS IN KCAL. AT 18° C.

The values are for the sum of the positive and negative ions per mole at infinite dilution.

Ion	F^-	Cl^-	Br^-	I^-
Li^+	246.6	208.8	199.9	189.1
Na^+	213.9	182.4	174.9	165.5
K^+	194.6	161.5	154.5	145.9
Rb^+	187.9	156.4	147.2	138.8
Cs^+	182.4	147.4	139.7	131.1
Ag^+	227.0	192.0	—	186.0
Cd^{++}	—	—	—	563.0

Born[8] has pointed out that, if the ions be considered as spheres of radius, r, and of charge, e, the energy of solution should be given by the expression

$$\Delta E = \left(\frac{e^2}{2r}\right)\left(1 - \frac{1}{D}\right),$$

where D is the dielectric constant of the solvent. This expression is derived by taking the difference in the energy of the electric field of the ion in a vacuum and in the solvent. From it one could obtain the absolute values for the energies of hydration of the individual ions but its application is difficult because of the uncertainty in the magnitude of the radii of the ions in aqueous solution. These radii differ from the crystal lattice values since they refer to the distance from the center of the ion to the center of the water dipole. This distance is further complicated by the fact that for positive ions the oxygen of the water is directed in, while for negative ions it is the hydrogen end of the dipole which is attracted. Another obvious difficulty is the inconstancy of the dielectric constant in the high electrical field of the ion.

However, it is a matter of considerable interest to obtain the individual ionic hydration energies, instead of the sums given in Table 4. A knowledge of the absolute potential of a single electrode would permit such a calculation. With this in mind, it is desirable to discuss the experimental determination of such potentials.

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[8] Born, M., Z. Physik, 1, 45 (1920).

Absolute electrode potentials. Probably the best determination of absolute potentials is given by the Lippmann capillary electrometer.[9] This makes use of the ingenious assumption that the surface tension of a mercury surface, in contact with an electrolyte, is a maximum when no potential difference exists between the metal and the electrolyte, *i.e.*, when there is no charge upon the mercury. The electrometer consists of two mercury electrodes, with a common electrolyte—for example, potassium chloride containing a small amount of calomel. For one of the electrodes, the contact between the electrolyte and the mercury is made through a capillary tube. If a potential is applied across this cell, the mercury in the capillary falls if that electrode is made positive, but if it is made negative, the column rises to a maximum of about 0.56 volts and then falls again at higher negative potentials. The interpretation given is that the mercury is normally positive to the solution and a potential of 0.56 volts is required to reduce it to the potential of the solution. If the height of the mercury in the capillary is plotted against the applied potential, one obtains a parabolic curve which is not quite symmetrical, indicating that the nature of the ion-absorption layer is different, depending upon whether it is positive or negative. A controversy has continued for many years as to the validity of the results. However, the evidence seems reasonably conclusive[10] that the absolute potential of the Hg–Hg_2Cl_2 couple must be fairly close to 0.56 volts.

Absolute hydration energies. This value may be used to calculate the energy of hydration of individual ions. Sodium will be used as an example. We have this result from the following equations:

	ΔF° *in kcal.*
$\mathrm{Hg} + \mathrm{Cl}^-(aq) = \frac{1}{2}\mathrm{Hg_2Cl_2} + e^-(\mathrm{Hg})$	12.9
$e^-(\mathrm{Hg}) = e^-(g)$	104.0[11]
$\frac{1}{2}\mathrm{Hg_2Cl_2} + \mathrm{Na}(s) = \mathrm{Hg} + \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq)$	−68.6[12]
$\mathrm{Na}(s) = \mathrm{Na}^+(aq) + e^-(g)$	48.3

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[9] Krüger, F., and Krumreich, H., Z. Elektrochem., **19**, 617 (1913).

[10] Cf. Baur, E., Z. Electrochem., **38**, 665 (1932).

[11] From the photoelectric long wave length limit. International Critical Tables, VI, 67.

[12] Cf. potentials for mercury and sodium, pp. 162 and 285 (Table 32).

The entropy[13] for this reaction is $\Delta S = 1$, hence $\Delta H^\circ = 48.6$ by equation (7) of Chapter I. Then for the following reactions we have:

	ΔH° *in kcal.*
$Na(s) = Na^+(aq) + e^-(g)$	48.6
$Na^+(g) + e^-(g) = Na(g)$	-119.4[14]
$Na(g) = Na(s)$	-26.0[15]
$Na^+(g) = Na^+(aq)$	-96.8

Having the hydration energy for a single ion, the values in Table 5 may be calculated from Table 4.

TABLE 5
APPROXIMATE VALUES FOR THE HYDRATION ENERGIES OF THE INDIVIDUAL IONS
In kcal. per mole.

Cs^+	63	Na^+	97
I^-	68	Ag^+	113
Rb^+	70	F^-	117
K^+	77	Li^+	123
Br^-	78	H^+	258
Cl^-	85	Cd^{++}	427

Factors which determine the magnitude of oxidation-reduction potentials. An analysis may now be made of the factors which determine whether a couple is electropositive or electronegative. Consider, for example, the question as to why sodium is a base metal and silver a noble metal.

	ΔH°		ΔH°
$Na(s) = Na(g)$	26	$Ag(s) = Ag(g)$	67
$Na(g) = Na^+(g) + e^-(g)$	118	$Ag(g) = Ag^+(g) + e^-(g)$	174
$Na^+(g) = Na^+(aq)$	-97	$Ag^+(g) = Ag^+(aq)$	-113
$Na(s) = Na^+(aq) + e^-(g)$	47 kcal.	$Ag(s) = Ag^+(aq) + e^-(g)$	128 kcal.

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[13] Latimer, W. M., Chem. Rev., **18**, 349 (1936).
[14] The ionization potential is corrected to ΔH_{298}.
[15] Sherman, J., Chem. Rev., **11**, 94 (1932).

These half-reactions as written contain the electrons as a gas, but that is unimportant for the comparisons. Since ΔH is positive, the larger positive value for the silver means a smaller tendency for the reaction to go, and this larger positive value is the result not only of the higher ionization potential but also the higher sublimation energy and is only slightly offset by the greater hydration energy.

Factors, then, which tend to make a metal noble are: (1) high ionization potential; (2) high sublimation energy, which is associated with high boiling point; and (3) low energy of hydration. In the case of silver, its noble character arises as much from the high value of factor (2) as from factor (1).

By subtraction one obtains,

$$\mathrm{Na} + \mathrm{Ag}^+ = \mathrm{Na}^+ + \mathrm{Ag} \qquad \Delta H^\circ = -81 \text{ kcal.}$$

Because the entropy change for the reaction is very small, the free energy is approximately equal to the heat of the reaction, $E^\circ = 3.5$ volts, in agreement with the measured reaction potential.

As another example, consider the relative oxidizing power of fluorine and iodine.

$$\begin{array}{rcll}
 & & & \Delta H^\circ \\
\tfrac{1}{2}\mathrm{F}_2(g) & = & \mathrm{F}(g) & 32 \\
\mathrm{F}(g) + e^-(g) & = & \mathrm{F}^-(g) & -92 \\
\mathrm{F}^-(g) & = & \mathrm{F}^-(aq) & -117 \\
\tfrac{1}{2}\mathrm{F}_2(g) + e^-(g) & = & \mathrm{F}^-(aq) & -177 \text{ kcal.}
\end{array}$$

$$\begin{array}{rcll}
\tfrac{1}{2}\mathrm{I}_2(s) & = & \mathrm{I}(g) & 26 \\
\mathrm{I}(g) + e^-(g) & = & \mathrm{I}^-(g) & -75 \\
\mathrm{I}^-(g) & = & \mathrm{I}^-(aq) & -68 \\
\tfrac{1}{2}\mathrm{I}_2(s) + e^-(g) & = & \mathrm{I}^-(aq) & -117 \text{ kcal.}
\end{array}$$

These equations show that fluorine is the better oxidizing agent, in part because of the higher electron affinity, but principally because of the greater energy of hydration of the smaller fluoride ion. In general, a large electron affinity, large energy of hydration, and small energy of formation of the monatomic gas atom from the standard state will favor a high oxidizing potential for elements forming negative ions.

An analysis of the factors which determine the oxidizing power of the oxygen acids and their compounds is more difficult. A half reaction, such as that for permanganate,

$$MnO_4^- + 8H^+ + 5e^- = Mn^{++} + 4H_2O,$$

can be broken up into a number of hypothetical steps:

1. Energy of dehydration of MnO_4^-.
2. Dissociation of MnO_4^- into Mn^{+7} and $4O^{--}$.
3. Energy of hydration of Mn^{++}.
4. Energy of union of H^+ and O^{--} to form water.
5. Ionization of Mn^{++} to Mn^{+7}.

It is obvious that low values for 1 and 2 and high values for the others will favor high oxidizing power but at present it is impossible to evaluate several of these steps accurately.

Proton affinities. The energy of the addition of a proton (hydrygen ion) to a negative ion or neutral molecule is called the proton affinity. Juza[16] has given the values summarized in Table 6. If one attempts to calculate these quantities as the coulombic energy of bringing two point charges, positive and negative, up to the known interatomic distances, the calculated energies are too small. Thus for HCl the calculated coulombic energy is about 250 kcal., and the experimental, 330 kcal. The difference represents the energy arising from the polarization of the negative ion or the energy of the bond (electron pair) forma-

TABLE 6
PROTON AFFINITIES
(All substances are gases.)

Reaction	kcal.
$N^{---} + H^+ = NH^{--}$	ca 820
$NH^{--} + H^+ = NH_2^-$	ca 650
$NH_2^- + H^+ = NH_3$	380
$NH_3 + H^+ = NH_4^+$	200
$O^{--} + H^+ = OH^-$	ca 640
$OH^- + H^+ = H_2O$	380
$H_2O + H^+ = H_3O^+$	170
$F^- + H^+ = HF$	370
$Cl^- + H^+ = HCl$	330
$Br^- + H^+ = HBr$	320
$I^- + H^+ = HI$	315

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[16] Juza, R., Z. anorg. allgem. Chem., **231**, 121 (1937).

tion. However, the coulombic picture is a very useful one in correlating the strength of the hydrogen compounds as acids. In general it may be stated: the ionization of the hydrogen acids increases (1) with increasing size of the negative ion, and (2) with decreasing charge on the negative ion. Thus HI is a stronger acid than HF and H_2S is stronger than H_2O because of the effect of the size. HF is stronger than H_2O because of the effect of the charge. It also follows that if the negative element forms hydrogen compounds of different oxidation states, the smaller the negative number of the oxidation state, the stronger will be the acid. Thus H_2O_2 is a stronger acid than H_2O and N_2H_4 is less basic than NH_3.

Acidic and basic oxides. The coulombic picture of the structure of oxides is also very useful in interpreting their acidic or basic properties. If the energy of attraction of a positive ion for oxide ion is small, the compound will ionize in water and since the oxide ion is completely hydrolyzed, hydroxide is formed. Thus for barium oxide,

$$\overset{(+2)}{\mathrm{Ba}}\mathrm{O} + \mathrm{H_2O} = \mathrm{Ba^{++}} + 2\mathrm{OH^-}.$$

On the other hand, if the attraction of the positive ion for oxide is very great it tends to take on additional oxides. For example in the case of sulfur trioxide,

$$\overset{(+6)}{\mathrm{S}}\mathrm{O_3} + \mathrm{H_2O} = \mathrm{SO_4^{--}} + 2\mathrm{H^+}.$$

Representing this attraction of the positive ion for the negative oxide as largely coulombic, one may then state: the smaller the radius of the positive ion and the larger its charge (oxidation state) the more acidic will be the oxide, and conversely, the larger the radius of the positive ion and the smaller its charge, the more basic will be the oxide.

This general principle is useful in correlating free energy changes with the periodic system. The only exceptions to the statement—that the heavier the member of a periodic family, the more basic its oxides—are to be found in the platinum metals. Here the energy of bond formation is so large that it overcomes the coulombic effect; and platinum oxide, for example, is less basic than nickel oxide.

It should be evident from the discussion that no direct relation exists between the nobility of a metal (oxidation potential) and the acidic or basic properties of its oxides.

CHAPTER III

Hydrogen

Hydrogen has but a single valence electron, and in the monatomic gas the electronic state is $s^1(^2S_{\frac{1}{2}})$. In addition to the isotope of mass one, molecular hydrogen and its compounds ordinarily contain appreciable quantities of the isotope of mass two, deuterium, and traces of the isotope of mass three. Thus ordinary water contains approximately one part in seven thousand of deuterium.[1] Because of the much greater percentage differences in the masses, these isotopes show a larger variation in their physical and chemical properties than do the isotopes of any other element. In fact, this is the only case where it will be necessary to consider differences in the thermodynamics of chemical reactions for two isotopes.

The standard state of the element is the diatomic molecule in the equilibrium mixture of the two molecular species, ortho- and para-. These molecules differ in the orientation of the spins of the two hydrogen nuclei; in the latter the spins are opposed and in the former, additive. At the temperature of liquid hydrogen the equilibrium mixture is almost completely parahydrogen, and at room temperatures the equilibrium mixture is an approximately 3 to 1 mixture of ortho- and para-. Giauque[2] has calculated 96,700 cal. as the free energy of dissociation into the atoms at 25° C. ΔS° for the reaction is 23.57 cal. per degree and ΔH°, 103,730 cal.

The energy of the deuterium molecule differs from that of hydrogen of mass one largely in the energy of the zero vibrational state. For H_2 the zero point energy is 6183 cal. and for D_2 it is 4394. The dissociation energy of D_2 is therefore 1.8 kcal. higher than that for H_2.[3]

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[1] Cf. Gabbard, J. L., and Dole, M., J. Am. Chem. Soc., **59**, 181 (1937); Lewis, G. N., and Macdonald, R. T., J. Chem. Phys., **1**, 341 (1933).

[2] Giauque, W. F., J. Am. Chem. Soc., **52**, 4828 (1930).

[3] Farkas, A., *Orthohydrogen, Parahydrogen and Heavy Hydrogen* (Cambridge University Press, 1935), p. 155.

Oxidation states. The oxidation states of hydrogen are +1 and −1. Acids and hydrogen ion are examples of the former. The compounds of hydrogen with highly electropositive elements, such as sodium and calcium, are true hydrides; and the oxidation state of the hydrogen is −1. In molten solution they give the hydride ion, H^-. This ion is oxidized at the anode upon electrolysis to molecular hydrogen.[4] The hydride ion has the electronic structure of helium and thus resembles the halides, all of which add one electron to form the noble gas type of ion. Between these two classes are many compounds, especially with carbon, in which two electrons are shared between the hydrogen and the other atom (covalence) and in which it is therefore ambiguous to talk of the oxidation state of the hydrogen. However, it is customary to refer to the oxidation state of hydrogen in all compounds except the true hydrides as +1 without raising the question of the distribution of the electrons in the bond.

The H_2—H^+ couple. As stated in Chapter I, the hydrogen couple is taken as the standard reference electrode, and its potential at unit fugacity of H_2 and activity of H^+ is arbitrarily set at zero.

$$H_2 = 2H^+ + 2e^-, \qquad E^\circ = 0.00$$

By equation (1) (Chap. I) the potential in volts of the couple at any pressure, P, in atmospheres of H_2 and at any concentration, C, of H^+ in moles per 1000 g of water at 25° C. is,

$$E = -0.05914 \log \frac{C_{H^+}}{P_{H_2}^{\frac{1}{2}}}.$$

This equation is a good approximation in dilute solutions and at low hydrogen pressures, but for exact calculations the thermodynamic concentration or activity and the thermodynamic pressure or fugacity must be used (cf. Chap. I).

For the interpretation of reactions in aqueous solutions, it is important to know the potential of the hydrogen couple in pure water and in 1 M OH^-. These values may be calculated from the ionization constant of water at 25° C. For this constant

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[4] Bardwell, D. C., J. Am. Chem. Soc., **44**, 2499 (1922).

Lewis and Randall give 1.005×10^{-14}, and Harned and Hamer[5] give 1.008×10^{-14}. We shall use the latter.

$$H_2O = H^+ + OH^-, \qquad K = 1.008 \times 10^{-14}$$

$$H_2 = 2H^+(10^{-7}M) + 2e^-, \qquad E = 0.414$$

$$H_2 + 2OH^- = 2H_2O + 2e^-, \qquad E^\circ = 0.828$$

From these values it follows that the reducing agent of a couple more positive than 0.414 should liberate hydrogen from water and of a couple more positive than 0.828 should liberate hydrogen from molal hydroxide solutions. In general then, it may be stated that the potential of the hydrogen couple may be correlated with the stability of reducing agents in water solutions. For example, of the two couples,

$$Sn^{++} = Sn^{++++} + 2e^-, \qquad E^\circ = -0.15$$

$$Cr^{++} = Cr^{+++} + e^-, \qquad E^\circ = 0.41,$$

it is obvious that Sn^{++} should not be oxidized by concentrated acid solution and that Cr^{++} is unstable in respect to the evolution of hydrogen even in low acid solutions.

The hydrogen couple is reversible, but the rate at which equilibrium is reached is generally slow. The reaction of acids with metallic zinc may be cited as an example of the slowness of hydrogen ion as an oxidizing agent. In this case, although there is a potential of 0.8 volts in favor of the oxidation of the zinc to zinc ion, there is no appreciable evolution of hydrogen with pure zinc in cold dilute acids. However if the zinc be touched with a piece of platinum, the reaction proceeds rapidly, with the evolution of the gas taking place on the surface of the platinum. In the electrolytic reduction of hydrogen at a cathode, it is possible to measure the excess voltage, over the reversible potential, which is required to liberate hydrogen. This excess voltage is termed overvoltage. Values for various experimental conditions are summarized in Table 7.[6]

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[5] Harned, H. S., and Hamer, W. J., J. Am. Chem. Soc., **55**, 2198 (1935).

[6] Table 7 is compiled from International Critical Tables, VI, 339; and from Handbuch der Physik, XIII, 564.

TABLE 7

OVERVOLTAGES OF HYDROGEN IN 1M H_2SO_4 IN VOLTS

(Current density in amperes per cm^2.)

Cathode	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1
Pt (black)	.003	.01	0.03	0.04	0.05
Pt	...	.02	0.07	0.29	0.68
Au	.12	.24	0.39	0.59	0.80
Fe	.22	.40	0.56	0.82	1.29
Cu	.35	.48	0.58	0.80	1.25
Pb	.45	.52	1.09	1.18	1.26
Zn	.55	.72	0.75	1.06	1.23
Ni	.20	.56	0.74	1.05	1.24
Cd	.65	.98	1.13	1.22	1.25
Hg	.60	.78	0.93	1.03	1.07
C	.29	.55	0.70	0.89	1.17
Ag	.30	.48	0.76	0.98	1.10
Al	.50	.57	0.83	1.00	1.29

It will be observed that the overvoltage depends upon the element used as cathode, its physical condition, and the current density. The lowest overvoltage is observed with platinized platinum surfaces. This substance is therefore used as electrodes to obtain reversible hydrogen potentials. At higher temperatures the magnitude of the overvoltage decreases, the change being 0.02 to 0.03 volts per each 10°. The net effect of the overvoltage phenomenon is to cause the hydrogen ion to act as though it were a much less powerful oxidizing agent, and hydrogen gas as though it were a much less powerful reducing agent, than the reversible potential would indicate.

The explanation of the slowness of hydrogen reactions is to be found in the reaction mechanism. Thus the first step in the reduction of the hydrogen ion would appear to be the formation of atomic hydrogen. The potential of the hydrogen atom–hydrogen ion couple may be calculated from the free energy of formation of atomic hydrogen, 48,350 cal.,

$$H = H^+ + e^-, \qquad E^\circ = 2.10$$

The union of two hydrogen atoms, of course, supplies energy for the net reaction but the very high positive value for this atomic hydrogen–hydrogen ion couple acts as a potential barrier which the electron must cross before the reaction can proceed. Gurney[7] has given a quantum mechanical treatment of the probability of the leakage of an electron across the barrier and has obtained an expression which shows the dependence of overvoltage on current density and temperature.

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[7] Gurney, R. W., Proc. Roy. Soc., **A 134**, 137 (1931).

However the problem has another important chemical factor, namely, the reaction of the atomic hydrogen with the electrode metal to form a surface layer. The greater the stability of such a compound the lower will be the potential of this couple and the lower the potential barrier.

$$\begin{array}{r@{\;=\;}l} 2XH & 2X + 2H^+ + 2e^- \\ 2XH & H_2 + 2X \\ \hline H_2 & 2H^+ + 2e^- \end{array}$$

The variation of hydrogen overvoltages with different metals will then depend upon the energy of formation of the surface hydrides. There is ample evidence for the formation of such hydrogen compounds, and the very high solubility of hydrogen in nickel, palladium, and platinum is associated with the catalysis of hydrogen (H_2) reactions by these metals and the low overvoltage for the cathodic reduction of hydrogen ion on their surfaces.

The decrease of the hydrogen-ion concentration has but slight effect upon the overvoltage until it becomes so low that the formation of a hydroxide coating upon the metal surface changes markedly the nature of the electrode.

The second ionization constant of water. The hydrolysis of oxide ion in water is so complete that no measurement of the concentration of the unhydrolyzed oxide ion can be made. A very rough estimate of the hydrolysis can be obtained from the ΔH° of solution of sodium oxide in water, -55 kcal. This heat is the sum of the true heat of solution of the oxide and the heat of hydrolysis. The corrected ΔH° of solution of sodium sulfide is -15.5 kcal. and we estimate that the true heat of solution of sodium oxide is not over -25 kcal. This would make the heat of hydrolysis greater than -30 kcal. The entropy of the hydrolysis is not large, so we may write,

$$O^{--} + H_2O = 2OH^-, \qquad K > 10^{22}$$

$$OH^- = O^{--} + H^+, \qquad K < 10^{-36}$$

The hydride-hydrogen ion couple. Hydride ion rapidly reduces water and is therefore unknown in aqueous solution. However, there are a number of calculations pertaining to the energy of the ion which are of interest. First, the free energies of the solid hydrides may be calculated, and from these the oxidation potentials of the solid hydrides determined. These calculations are summarized in Table 8.

TABLE 8

FREE ENERGIES AND POTENTIALS OF SOLID HYDRIDES

Hydride	$\Delta S°$	$\Delta H°$	$\Delta F°$	Free energy of metal ion	$MH_n = M^{n+} + \frac{n}{2}H_2 + ne^-$ $E°$
CaH_2	−31.2	−46,000	−36,700	−132,700	2.13
SrH_2	−31.2	−42,100	−32,800	−133,200	2.18
BaH_2	−31.2	−40,800	−31,500	−133,850	2.22
LiH	−15.6	−21,540	−16,900	−70,700	2.33
NaH	−15.6	−14,000	−9,300	−62,590	2.31
KH	−15.6	−10,000	−5,300	−67,430	2.69
RbH	−15.6	−12,000	−7,300	−68,800	2.66
CsH	−15.6	−12,000	−7,300	−70,280	2.73
ThH_4	−62.5	42,800	61,500	−197,100	2.80

Only the entropy of calcium hydride has been accurately obtained experimentally, and in this case the entropy of the hydride is almost identical with that of the metal. In calculating the $\Delta S°$ of formation for the other hydrides, the assumption has been made that the same relation holds true as a close approximation. $\Delta H°$ values are from Bichowsky and Rossini and the free energies of formation of the metal ions are taken from later chapters.

The $E°$ values, summarized in the last column of Table 8, are of the same order of magnitude and the differences may be interpreted as arising from the different solubilities of the various hydrides. Before discussing these, we shall calculate an approximate value of the H^-—H_2 couple from the electron affinity, ionization potentials, and related data, in the following manner:

$$
\begin{array}{rcl|r}
 & & & \Delta H(kcal.) \\
H_2 & = & 2H & 104 \\
H & = & H^+(g) + e^- & 312 \\
H + e^- & = & H^-(g) & 1.8 \\
H^+(g) & = & H^+(aq) & -258 \\
H^-(g) & = & H^-(aq) & -117 \\
\hline
H_2 & = & H^+(aq) + H^-(aq) & 42.8
\end{array}
$$

With the exception of the heat of hydration of the hydride ion which has been estimated as the same as that for fluoride ion, these data have been taken from Chapter II. This assumption is based upon the similarity of the ionic radii, although hydride is probably somewhat larger than fluoride. Continuing the analogy of hydride and fluoride, we estimate the entropy of hydride ion to be approximately 2.0. Hence ΔS° is -29.2 cal. per degree and ΔF° is 51,500 cal. One then computes,

$$H^- = \tfrac{1}{2}H_2 + e^-, \qquad E^\circ = 2.23$$

From the nature of the calculation, the E° may be in error by several tenths of a volt. If it is correct, it would mean, by reference to Table 8, that the alkali hydrides are fairly soluble and those of the alkaline earth metals less so. In these solubility relations, the hydrides appear to resemble the fluorides of these elements more than the chlorides. Because of the high positive value of the couple, true hydrides are formed only by metals whose potentials are greater than 2 volts.

The work of Sollers and Crenshaw[8] on the dissociation pressures of sodium and potassium deuteride may be used as a basis for similar calculations on the potential of the deuteride ion.

The D_2—D^+ couple. A direct measurement of the deuterium gas-deuterium ion couple cannot be made in water solution because of the rapid interchange of the deuterium atoms with the hydrogen. However, Abel, Bratu, and Redlich[9] were able to compare the deuterium couple in pure deuterium oxide with the hydrogen couple in water, through a common reference electrode. These authors reported,

$$D_2 = 2D^+ + 2e^-, \qquad E^\circ = 0.0034,$$

and for the ionization constant of the "heavy" water,

$$D_2O = OD^- + D^+, \qquad K = 0.3 \times 10^{-14}$$

The smaller energy of the lowest vibrational state in D_2, as compared to H_2, has been mentioned above, and in general the bond between deuterium and another atom is slightly stronger than the corresponding bond with hydrogen. The lower ionization constant of D_2O is in line with this statement.

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[8] Sollers, E. F., and Crenshaw, J. L., J. Am. Chem. Soc., **59**, 2015 and 2724 (1937).

[9] Abel, E., Bratu, E., and Redlich, O., Z. physik. Chem., **A 170**, 153 (1934); **A 173**, 353 (1935).

When an alkaline solution of water containing deuterium is electrolyzed, an enrichment of the deuterium occurs. The enrichment factor, that is, the percentage loss of hydrogen to the percentage loss of deuterium, is around 5 to 8 in general practice, using nickel and iron cathodes. This preferential reduction of H^+ obviously involves both the equilibrium and overvoltage potentials and the rate of interchange of the intermediate monatomic hydrogen and deuterium on the metal surface with the atoms of the solution. The greater ionization of the hydrogen is doubtless a most important factor. Novak[10] reported the D_2 overvoltage in 99.6 per cent D_2O with a mercury cathode to be 0.087 volts greater than that for H_2 with similar current density. Heyrovsky[11] and Halpern and Gross[12] have discussed the theory of the enrichment factor.

The following equilibrium constants involving hydrogen and deuterium have been quoted by Farkas and Farkas:[13]

$$H_2 + D_2 = 2HD, \qquad K = 3.27$$

$$H_2O + D_2O = 2HDO, \qquad K = 32.7$$

$$H_2O + HD = HDO + H_2, \qquad K = 3.8$$

For the equilibrium involving hydrogen ion and deuterium ion, Hamill[14] calculates

$$H^+ + HDO = D^+ + H_2O, \qquad K = 0.141$$

These authors have discussed the general problem of the complicated equilibria in light and heavy water solutions in some detail.

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[10] Novak, J., Coll. Czechoslov. Chem. Commun., **9**, 207 (1937).
[11] Heyrovsky, J., Coll. Czechoslov. Chem. Commun., **9**, 273 (1937).
[12] Halpern, O., and Gross, P., J. Chem. Phys., **3**, 452 (1935).
[13] Farkas, A., and Farkas, L., J. Chem Phys., **2**, 468 (1934).
[14] Hamill, W. H., J. Am. Chem. Soc., **59**, 1494 (1937).

CHAPTER IV

Oxygen

Oxygen has six valence electrons, and in the monatomic gas atoms the lowest electronic state is $s^2p^4(^3P_2)$. Because of the importance of oxygen in the chemistry of water solutions, its potentials and free energies will be considered in advance of the other members of the group.

The standard thermodynamic state of the element is the gas O_2. Bichowsky and Rossini[1] gave 118.2 kcal. as the heat of dissociation. This, combined with the entropy of dissociation (27.33 cal. per degree), gives 110,050 cal. as the free energy of dissociation. The element also exists as the gaseous molecule, O_3, ozone. From the heat of formation (34.5 kcal.) and the entropy of formation (4.9 cal. per degree) the free energy of ozone is 39.4 kcal. At low temperatures the modification O_4 appears to be formed.[2]

The isotopes 17 and 18 are present in small amounts in all oxygen; however, these differ from oxygen 16 by such small energies that for all ordinary thermodynamics their presence may be ignored.

Oxidation states. In water, and all true oxides and their compounds, oxygen has the oxidation number of -2. The oxidation state in hydrogen peroxide and its salts and the peroxide oxygen of the peroxyacids is -1. This same state should be assigned to the oxygen in free hydroxyl, OH, which does not exist in appreciable concentrations but which does appear to be formed as an intermediate step in a number of reactions. In the compound HO_2 and its derivatives, as KO_2, the oxygen has an average oxidation number of $-\frac{1}{2}$, which might be interpreted as one oxide oxygen and one $+1$ oxygen. Because of the highly electronegative character of fluorine, the oxygen fluoride, OF_2, may logically be considered as having oxygen in the $+2$ state, and there is some evidence of the existence of the corresponding acid H_2O_3.

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[1] Bichowsky, F. R., and Rossini, F. D., *Thermochemistry of the Chemical Substances* (Reinhold, New York, 1936), p. 19.

[2] Lewis, G. N., J. Am. Chem. Soc., **46**, 2027 (1924).

The water-oxygen couple. Probably the best value for the free energy of formation of liquid water is that calculated from the third law, using the Bichowsky and Rossini heat of formation, −68,320 cal. (corrected to 25° C.), and the entropy of formation, −39.0 cal. per degree. This gives,

$$\tfrac{1}{2}O_2 + H_2 = H_2O, \qquad \Delta F^\circ = -56{,}690 \text{ cal.}$$

From the free energy of vaporization, 2054 cal., given by Kelley,[3] the free energy of $H_2O(g)$ at 25° C. is −54,636 cal. One then calculates for the oxygen couple in acid solution,

$$2H_2O = O_2 + 4H^+ + 4e^-, \qquad E^\circ = -1.229;$$

in alkaline solution,

$$4OH^- = O_2 + 2H_2O + 4e^-, \qquad E^\circ_B = -0.401;$$

and in pure water,

$$2H_2O = O_2 + 4H^+(10^{-7}M) + 4e^-, \qquad E = -0.815.$$

From the free energy of ionization of water, the free energy of formation of OH^- is −37,585 cal.

These potentials have the same importance in reference to the stability of oxidizing agents in water solution that those for hydrogen have to the stability of reducing agents (cf. Chap. III). Thus, the oxidized form of any couple with a higher negative potential than oxygen, at a given concentration of hydrogen ion, should liberate oxygen from the solution. For example, this is true for the manganous-permanganate couple,

$$4H_2O + Mn^{++} = MnO_4^- + 8H^+ + 5e^-, \qquad E^\circ = -1.52$$

and hence permanganate is unstable in acid solution with respect to oxidation of the water to oxygen. However, the oxygen couple is highly irreversible and in general it is impossible to obtain experimental equilibrium involving the couple. For the discussion of the so-called "oxygen electrode" see the hydrogen peroxide-oxygen couple. As a result of this irreversibility, high overvoltages are required for the liberation of oxygen from water. In Table 9 there are given values of the overvoltages required for the anodic oxidation of water on various electrode surfaces.[4]

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[3] Kelley, K. K., U. S. Bur. Mines Bull., 383 (1935).

[4] International Critical Tables, VI, 339.

TABLE 9

OXYGEN OVERVOLTAGES IN VOLTS FOR VARIOUS ANODES IN 1 *M* KOH

(Current density in amperes per cm².)

Anode	0.01	0.1	1.0
Graphite	0.52	1.09	1.24
Au	0.67	1.24	1.68
Cu	0.42	0.66	0.84
Ag	0.58	0.98	1.14
Pt (smooth)	0.72	1.28	1.38
Pt (black)	0.40	0.64	0.79
Ni	0.35	0.73	0.87

These potentials are not very reproducible, and for the more electropositive metals in the list they are attainable only because the metal surface becomes coated with an oxide layer which renders it passive; otherwise the metals would be oxidized instead of the water, since their oxidation potentials are smaller. In acid solutions it is impossible, because of the high potential required, to measure oxygen overvoltage except for the very noble metals. For smooth platinum, the acid values are about the same as in the alkaline, being 0.45 volts for the formation of the first oxygen bubbles.

A number of theories have been advanced in explanation of the oxygen overvoltage and the mechanism of the oxidation of water or hydroxide, but definite experimental proof is lacking for the support of any one view.

The assumption is frequently made that the first and rate-determining step is,

$$OH^- = OH + e^-,$$

or in acid solution,

$$H_2O = OH + H^+ + e^-.$$

However, the potentials of these reactions are so large (cf. hydroxyl) that, even with the high overvoltage, the concentration of OH must be very small. Glasstone and Hickling[5] believe that the second reaction,

$$2OH = H_2O_2,$$

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[5] Glasstone, S., and Hickling, A., Trans. Faraday Soc., **31**, 1656 (1935).

occurs and O_2 is formed by the catalytic decomposition of the hydrogen peroxide. However, there is but little experimental proof of the formation of the peroxide at an electrode. Walker and Weiss[6] supposed that the second reaction is,

$$2OH = H_2O + O,$$

followed by the formation of molecular oxygen.

The author believes that an equally plausible mechanism is the preliminary oxidation of the anode metal to some surface oxide or hydroxide, which then reacts as indicated by the following hypothetical equation,

$$XO_2 + OH^- = XOH + O_2 + e^-,$$

or if peroxide is an intermediate product, a reaction such as,

$$X(OH)_2 + OH^- = XOH + H_2O_2 + e^-.$$

Probably no one mechanism can be given to include all types of electrodes and electrolytes. The latter is certainly important, as the oxidation of the negative ion doubtless enters into the mechanism in a number of cases (cf. also mechanism of hydrogen overvoltage).

Noyes and his co-workers[7] give support to the peroxide theory. They found in their study of the oxidation of water by + 2 silver in acid solutions, that their rate law was best explained by the assumption that the formation of peroxide was the rate-determining process.

The water-oxygen atom couple. From the free energy of atomic oxygen (55,025 cal.) and the free energy of water, one calculates for the reduction of the atom to water in acid solution,

$$H_2O = O(g) + 2H^+ + 2e^-, \qquad E^\circ = -2.42$$

The high negative value for the potential indicates the difficulty in the oxidation of water with the formation of atomic oxygen as an intermediate step.

The peroxide-oxygen couple. However meager the evidence may be for the oxidation of water to peroxide, there is abundant proof that oxygen in the presence of hydrogen ion is generally, if not always, reduced to hydrogen peroxide, possibly with the formation of HO_2 as an intermediate step with some reducing agents (vide infra). Lewis and Randall[8] give for the free energy of $H_2O_2(aq)$, −31,470 cal., and for HO_2^-, −15,610 cal.

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[6] Walker, O. J., and Weiss, J., Trans. Faraday Soc., **31,** 1011 (1935).

[7] Cf. Noyes, A. A., Coryell, C. D., Stitt, F., and Kossiakoff, A., J. Am. Chem. Soc., **59,** 1316 (1937).

$$H_2O_2 = H^+ + HO_2^-, \qquad K = 2.4 \times 10^{-12}$$

From these values one calculates for the reduction of oxygen to peroxide in acid and alkali,

$$H_2O_2 = O_2 + 2H^+ + 2e^-, \qquad E^\circ = -0.682$$

$$OH^- + HO_2^- = O_2 + H_2O + 2e^-, \qquad E^\circ_B = 0.076$$

Although many of the experimental attempts to determine the reversible potential of the oxygen electrode appear to have measured merely the potential of the platinum-platinum oxide couple which is in the neighborhood of one volt, Bornemann,[9] has shown that it is possible to obtain a value for the reversible potential of the H_2O_2–O_2 couple by cell measurements. He reported for E° in acid solution, -0.66 ± 0.03 volts, which is in agreement with the value given above. The ability to determine this couple in the presence of the H_2O—H_2O_2 couple, with its much higher potential, $E^\circ = -1.77$, shows that the activation energy of the oxygen molecule must be quite low.

The above potentials account for the slowness of many direct oxidations by O_2. If the reaction must go through peroxide, the low potential of this reaction makes it the rate-determining step. Thus, for example, in the oxidation of ferrous ion in acid solution,

$$Fe^{++} = Fe^{+++} + e^-, \qquad E^\circ = -0.77$$

the couple O_2—H_2O with a voltage of 1.23 has sufficient energy to effect the oxidation of the ferrous ion; but if the initial step is O_2—H_2O_2 with a voltage of 0.68, the oxidation can proceed only slowly (see also Table 10, p. 42, for the mechanism through HO_2).

It is also apparent from these potentials that strong oxidizing agents will oxidize hydrogen peroxide to oxygen. However, the potential of the H_2O_2—H_2O couple is itself so high (vide infra) that it can generally oxidize the reduced form of the other oxidizing agent, so that the net result is simply the catalytic decomposition of the hydrogen peroxide.[10]

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[8] Lewis, G. N., and Randall, M., *Thermodynamics* (McGraw-Hill, New York, 1923), p. 487.

[9] Bornemann, K., *Nernst Festschrift* (Knapp, Halle, 1912), p. 118.

EXAMPLE

$$\begin{array}{r}
Br_2 + H_2O_2 = 2H^+ + 2Br^- + O_2 \\
\underline{H_2O_2 + 2Br^- + 2H^+ = Br_2 + 2H_2O \quad\;} \\
2H_2O_2 = O_2 + 2H_2O \quad\;
\end{array}$$

In a few cases, however, the peroxide can be oxidized quantitatively, as, for example, by permanganate.

The water-peroxide couple. From free energy data for peroxide given above, one calculates for the water-hydrogen peroxide couple in acid solution,

$$2H_2O = H_2O_2 + 2H^+ + 2e^-, \qquad E^\circ = -1.77$$

In alkaline solution this becomes

$$3OH^- = HO_2^- + H_2O + 2e^-, \qquad E^\circ_B = -0.87$$

These high negative values place peroxide in the group of the most powerful oxidizing agents in both acid and alkaline solution. It is, of course, unstable in respect to the oxidation of water, but more important is its instability in respect to its own oxidation and reduction. In acid solution,

$$2H_2O_2 = 2H_2O + O_2, \qquad \Delta F^\circ = -50{,}440 \text{ cal.}$$

and in alkaline solution,

$$2HO_2^- = 2OH^- + O_2, \qquad \Delta F^\circ = -43{,}950 \text{ cal.}$$

The reaction rates are slow but are catalyzed by many substances which are constituents of couples with potentials lying between the oxidation and reduction potentials of peroxide as indicated in the bromide-bromine example given above. Catalysis is also effected by many solids and enzymes.

The free energy of solid peroxides. Most of the more electropositive metals form true peroxides. The third law may be employed to calculate their free energies. As there are no experimental values for the entropies of the oxides, these must be estimated; but the errors in these estimated quantities should not exceed 500 cal. Thus, for the formation of calcium peroxide, CaO_2, $\Delta H°$ is $-156,400$ cal.; $\Delta S°$, -47 cal. per degree (estimated); and $\Delta F°$, $-142,000$ cal. Similarly, we find for the free energies in calories of the following: SrO_2, $-139,000$ cal.; BaO_2, $-138,000$ cal.; Li_2O_2, $-138,000$ cal.; and Na_2O_2, $-105,000$ cal.

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[10] Cf. Bray, W. C., and Livingston, R. S., *J. Am. Chem. Soc.*, **45**, 1251 (1923).

These free energies determine the potentials of the oxides as oxidizing and reducing agents. Although these couples are not thermodynamically reversible, since the unhydrated oxides do not exist in equilibrium with water, they are of interest for the purpose of comparing the energies of the oxides. The hydroxide-peroxide potentials in alkaline solution are summarized below:

$$4OH^- + nM^{\frac{2+}{n}} = M_nO_2 + 2H_2O + 2e^-.$$

E_B°:Ca, -0.60; Sr, -0.67; Ba, -0.71; Li, -0.85; Na, -1.23. These potentials differ from the -0.87 value for the OH^- — HO_2^- couple by the free energy of the hydrolysis of the O_2^{--} ion and by the free energy of solution of the peroxide. The first of these is quite large, since the second dissociation constant of H_2O_2 must be around 10^{-25}, and it is a constant factor. The increasing oxidizing power in the series CaO_2 to Na_2O is due then to the increasing solubility of the peroxides, which is obviously in the same order as the basicity of the hydroxides.

The water, oxygen-ozone couple. The action of ozone as an oxidizing agent is unusual in that ordinarily only one of the oxygens is reduced, the other two atoms forming molecular oxygen. From the free energy of ozone and water given above, one calculates for the couple in acid solution,

$$O_2 + H_2O = O_3 + 2H^+ + 2e^-, \qquad E° = -2.07$$

In alkaline solution this becomes,

$$O_2 + 2OH^- = O_3 + H_2O + 2e^-, \qquad E_B^\circ = -1.24$$

These high values place ozone next to fluorine in the list of powerful oxidizing agents, with the exception, of course, of a few substances like atomic oxygen which do not exist in appreciable concentrations at room temperature. It is unstable with respect to the decomposition into oxygen, and the catalysis of this reaction in water is a subject of considerable controversy. Many of the points involved are discussed in the following paragraphs.

Couples involving perhydroxyl.[11] It is logically assumed in the kinetics of oxygen reactions that the addition of atomic hydrogen to the oxygen molecule or the removal of one electron from the molecule in acid solution results in the formation of perhydroxyl, HO_2. The compound KO_2 (formerly considered K_2O_4)[12] is, of course, the potassium salt of perhydroxyl, and there is considerable evidence of the formation of the ion O_2^- when ozone is passed into concentrated alkali solution;[13] but the comparative stability of ozone in acid solution indicates that the free energy is unfavorable for the reaction in the presence of hydrogen ion. On this basis the free energies of formation of HO_2 and O_2^- have been estimated as 3000 and 13,000 cals., respectively. The difference of 10,000 cal. is an estimated free energy of ionization of HO_2. These values then give,

$$O_3 + H_2O = 2HO_2, \qquad \Delta F^\circ = 23.3 \text{ kcal.}$$

$$O_3 + 2OH^- = 2O_2^- + H_2O, \qquad \Delta F^\circ = 5.1 \text{ kcal.}$$

Using these free energies of formation with that of hydrogen peroxide, the perhydroxyl-hydrogen peroxide couples then are,

$$H_2O_2 = HO_2 + H^+ + e^-, \qquad E^\circ = -1.5$$

$$OH^- + HO_2^- = O_2^- + H_2O + e^-, \qquad E^\circ_B = -0.4$$

These potentials lie between the values calculated from the energies of the reactions by Weiss[14] and the earlier work by Haber and Weiss.[15] They can hardly be more negative and still have the $F^\circ_{O_2^-}$ be small enough to give an appreciable concentration of O_2^- by the action of ozone on concentrated hydroxide, but they might be as high as -1.3 and -0.2.

Perhydroxyl is unstable in acid with respect to the decomposition into ozone and water, $\Delta F^\circ = -23.3$ kcal., as given above, but it is also unstable with respect to the decomposition into hydrogen peroxide and oxygen.

$$2HO_2 = H_2O_2 + O_2, \qquad \Delta F^\circ = -37.5 \text{ kcal.}$$

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[11] No name has been adopted by general usage for the compound HO_2. The author proposes to call it *perhydroxyl*; that is, two oxygens in place of the one in hydroxyl.

[12] Neuman, E. W., J. Chem. Phys., **2**, 31 (1934).

[13] Weiss, J., Trans. Faraday Soc., **31**, 668 (1935).

[14] *Ibid.*

[15] Haber, F., and Weiss, J., Proc. Roy. Soc., **A 147**, 332 (1934).

This is the more probable of the two decompositions, and experimentally KO_2 rapidly gives a practically quantitative yield of these products when treated with acid, although a trace of ozone may be formed. Since hydrogen peroxide is a rapid catalyst for the decomposition of ozone into oxygen, these facts rule out the possibility of the formation of any appreciable concentration of HO_2 by the action of ozone on water in acid.

The free energy is favorable for the oxidation of water to perhydroxyl by ozone through the reaction,

$$3O_3 + H_2O = 2HO_2 + 3O_2, \qquad \Delta F^\circ = -55.5 \text{ kcal.}$$

However the reaction mechanism involving three ozone molecules might easily lead to a very slow reaction rate. The free energy is also favorable for the oxidation of hydrogen peroxide to perhydroxyl by ozone.

$$O_3 + 2H_2O_2 = 2HO_2 + H_2O + O_2, \qquad \Delta F^\circ = -27.1 \text{ kcal.}$$

The half-reactions for the reduction of perhydroxyl to water and hydroxide are,

$$2H_2O = HO_2 + 3H^+ + 3e^-, \qquad E^\circ = -1.7$$

$$4OH^- = O_2^- + 2H_2O + 3e^-, \qquad E^\circ_B = -0.7$$

and for the perhydroxyl-oxygen couples,

$$HO_2 = O_2 + H^+ + e^-, \qquad E^\circ = 0.1$$

$$O_2^- = O_2 + e^-, \qquad E^\circ_B = 0.6$$

In order to complete the series for the reduction of oxygen in steps, the potentials for the perhydroxide-perhydroxyl should be given. These values are summarized in Table 10.

TABLE 10
REDUCTION OF OXYGEN IN STEPS

(a) Acid solution:	E°
$HO_2 = O_2 + H^+ + e^-$	0.1
$H_2O_2 = HO_2 + H^+ + e^-$	−1.5
$2H_2O = H_2O_2 + 2H^+ + 2e^-$	−1.77
(b) Basic solution:	E°_B
$O_2^- = O_2 + e^-$	0.6
$OH^- + HO_2^- = O_2^- + H_2O + e^-$	−0.41
$3OH^- = HO_2^- + H_2O + 2e^-$	−0.87

Couples involving hydroxyl. There is evidence of the existence of free hydroxyl, OH, in gaseous reactions involving hydrogen and oxygen and their compounds, and it is frequently assumed as an intermediate step in the oxidation of water. Using the value of Bates[16] for the heat of formation of OH gas, and the approximate entropy, one obtains the ΔF° value for the gas. Making the probable assumption that the free energy of solution is small, the free energy of formation and the resulting potentials for hydroxyl in aqueous solutions are,

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}O_2 = OH, \qquad \Delta F^\circ = -5.0 \text{ kcal.}$$

$$H_2O = OH + H^+ + e^-, \qquad E^\circ = -2.2$$

$$OH^- = OH + e^-, \qquad E^\circ_B = -1.4$$

Corresponding to these values, the potentials of hydroxyl as a reducing agent are,

$$OH = \tfrac{1}{2}O_2 + H^+ + e^-, \qquad E^\circ = -0.22$$

$$OH + OH^- = \tfrac{1}{2}O_2 + H_2O + e^-, \qquad E^\circ_B = 0.61$$

The free energy is favorable for the union of two hydroxyls to form hydrogen peroxide,

$$2OH = H_2O_2, \qquad \Delta F^\circ = -21 \text{ kcal.}$$

The energy is not very large and there is no experimental evidence to show that the speed of the reaction is rapid.

For the reaction of two hydroxyls to form water and atomic oxygen,

$$2OH = H_2O + O, \qquad \Delta F^\circ = 8.3 \text{ kcal.}$$

The free energy indicates that the formation of atomic oxygen would not be appreciable unless the concentration of hydroxyl were large.

The oxidation of water by ozone to hydroxyl,

$$O_3 + H_2O = 2OH + O_2, \qquad \Delta F^\circ = 7.3 \text{ kcal.}$$

has, from this free energy, an equilibrium constant, $K = 4 \times 10^{-6}$. The equilibrium concentration of OH is thus quite small, but the mechanism of the reaction should be very simple, and this reaction, therefore, may account for the slow decomposition of ozone in acid solutions. However, another possible mechanism for the ozone decomposition is the slow formation of H_2O_2 which, in turn, catalyzes the decomposition of the ozone.

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[16] Bates, J. R., J. Chem. Phys., **1**, 457 (1933).

$$O_3 + H_2O = H_2O_2 + O_2, \qquad \Delta F^\circ = -14 \text{ kcal.}$$

Bray[17] suggests from a study of the rate of the catalytic decomposition of ozone by hydrogen peroxide that the essential mechanism may be,

$$\begin{array}{c} O_3 + H_2O_2 = H_2O_3 + O_2 \\ \underline{O_3 + H_2O_3 = H_2O_2 + 2O_2} \\ 2O_3 = 3O_2 \end{array}$$

If this is correct, the free energy of the compound H_2O_3, in order to permit the reaction to proceed, must be close to zero, $F^\circ_{H_2O_3} = 0$. This value would then give,

$$3H_2O = H_2O_3 + 4H^+ + 4e^-, \qquad E^\circ = -1.8$$

and for H_2O_3 as a reducing agent to form oxygen,

$$H_2O_3 = \tfrac{2}{3}O_3 + 2H^+ + 2e^-, \qquad E^\circ = -0.6$$

As additional evidence of the existence of H_2O_3, reference should be given to the preparation of K_2O_3 by Kraus and Whyte.[18]

These potentials, and equally well the potentials for hydroxyl and perhydroxyl, must be considered as strictly tentative.

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[17] Bray, W. C., J. Am. Chem. Soc., **60,** 82 (1938).

[18] Kraus, C. A., and Whyte, E. F., J. Am. Chem. Soc., **48,** 1788 (1926).

CHAPTER V

The Halogens

The members of the halogen family have seven valence electrons, and in the monatomic gas atoms the electronic state is $s^2p^5(^2P_{\frac{3}{2}})$. The outer shell of the kernel contains the following electrons: fluorine, $1s^2$; chlorine, $2s^2$, $2p^6$; bromine, $3s^2$, $3p^6$, $3d^{10}$; and iodine, $4s^2$, $4p^6$, $4d^{10}$. The principal oxidation states are -1, $+1$, $+3$, $+5$, and $+7$, the lowest energy being that of the -1 state. In this sense the halogens as a group are the most electronegative of all the elements. Not only the free elements but the oxygen acids and their salts are powerful oxidizing agents with respect to their reduction to the halide (-1 state). The -1 ion has the same electron structure as the following noble gas, and the tendency to form this ion may be correlated with the stability of this electronic structure.

Fluorine

The standard state of the free element is the gas molecule, F_2. The heat of dissociation into atoms is 63.5 kcal., and the entropy of dissociation is 27.9 cal. per degree; hence the free energy of F(g) is 27.6 kcal. The only oxidation state stable in water solutions is the -1. The oxides, F_2O and F_2O_2, have been prepared, but because of the highly electronegative character of both fluorine and oxygen, it is meaningless to attempt to assign a polar number to fluorine in these compounds. However, the oxides are powerful oxidizing agents and the potential for the reduction of the monoxide may be calculated.

The fluoride-fluorine couple. The potential of this couple has been calculated by Latimer[1] from thermal data by Wartenberg[2] on the reaction of fluorine with hydrogen and the replacement of chloride by fluorine. Bichowsky and Rossini have used the Wartenberg data to calculate the heat of formation of fluoride ion,

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[1] Latimer, W. M., J. Am. Chem. Soc., **48**, 2868 (1926).

[2] Wartenberg, H. v., Z. anorg. allgem. Chem., **151**, 313 (1926).

-78.2 kcal. From this value and slightly revised entropy data, the potential has been recalculated, but the result is the same as the former figure. The ΔF° of formation of the ion is $-65{,}700$ cal. and the potential,

$$2F^- = F_2 + 2e^-, \qquad E^\circ = -2.85$$

In acid solutions the couple should be written with HF or H_2F_2. Pick[3] gave

$$HF(aq) = H^+ + F^-, \qquad K = 7.2 \times 10^{-4}.$$

At high concentrations he assumed HF_2^- was formed and wrote

$$F^- + HF = HF_2^-, \qquad K = 5.5.$$

The free energy of HF then is $-70{,}000$ cal. and for the HF—F_2 couple,

$$2HF(aq) = F_2 + 2H^+ + 2e^-, \qquad E^\circ = -3.03.$$

This is the highest potential for any oxidizing agent which can be prepared in appreciable concentrations. The potential is so high that fluorine decomposes water with the evolution of oxygen and ozone.

The fluorine-oxide potential. Bichowsky and Rossini give as the best value for the heat of formation of the gaseous oxide, $+5.5$ kcal. From the interatomic distances the entropy of F_2O is approximately 59 cal. per degree. One may then calculate, $\Delta F^\circ = 9.5$ kcal., and

$$H_2O + 2F^- = F_2O + 2H^+ + 4e^-, \qquad E^\circ = -2.1.$$

A potential may also be calculated for the reduction to fluoride ion and free oxygen,

$$2F^- + \tfrac{1}{2}O_2 = F_2O + 2e^-, \qquad E^\circ = -3.1.$$

The potential of this reaction is even higher than that for fluoride, but it doubtless is impossible of experimental realization since the first step is the formation of atomic oxygen while much of the energy comes from the union of oxygen atoms to form the O_2 molecule. This would give a potential barrier which would render the reaction rate very slow.

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[3] Pick, H., *Nernsts Festschrift* (Knapp, Halle, 1912), p. 360.

Chlorine

The stable state of the element at room temperature is the diatomic molecule, Cl_2. The heat and free energy of dissociation into the atoms are ΔH°, 57.8 kcal. and ΔF°, 51.8 kcal. The free energy of solution to form a hypothetical one molal solution is[4] 1.6 kcal.

Oxidation states. Chlorine has an oxidation number of -1 in hydrochloric acid and its salts; $+1$ in the oxide, Cl_2O, in its acid, hypochlorous acid, $HClO$, and its salts; $+3$ in chlorous acid, $HClO_2$, and its salts; $+4$ in the dioxide, ClO_2; $+5$ in chloric acid, $HClO_3$, and derivatives; and $+7$ in the oxide, Cl_2O_7, in perchloric acid, $HClO_4$, and the perchlorates. The oxide, ClO, is described, but its chemistry is so uncertain that it has not been included in the calculation of potential values.

The chloride-chlorine couple. The best value for the potential of the Cl^-—Cl_2 couple is probably that obtained from the cell measurements of this electrode against the AgCl—Ag electrode. We shall use the value given by Randall and Young,[5] which appears to be accurate to two or three millivolts.

$$2Cl^- = Cl_2 + 2e^-, \qquad E^\circ = -1.3583.$$

This corresponds to a free energy of formation of chloride ion of $-31{,}330$ cal. Because of the hydrolysis of chlorine and the formation of hypochlorite, the potential becomes meaningless in alkaline solutions. The couple is reversible and chlorine is a fairly rapid oxidizing agent, very much faster than oxygen, for example. Because of the mechanism of formation of the Cl_2 molecule by oxidation of the Cl^-, overvoltages must exist (cf. overvoltage of hydrogen and oxygen), and Knobel[6] gives the values at 100 milliamperes per cm^2 of 0.026 volts for platinized platinum and 0.054 for smooth platinum. The problem is complicated by the fact that the oxidation potential of water is lower than that for chloride, hence, were it not for the high oxygen overvoltage, no chlorine should be evolved upon the electrolysis of chloride solutions at low current densities. In other words, the chlorine overvoltages must always be measured on an electrode which is polarized with respect to oxygen. The mechanism is doubtless complex and may involve the formation of hypochlorite surface compounds which react with chloride to give chlorine. The ratio of oxygen to chlorine evolution is also influenced by the presence of positive ions, for example, Mn^{++}, which catalyze one or other of the oxidations.

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[4] International Critical Tables, VII, 233.

[5] Randall, M., and Young, L. E., J. Am. Chem. Soc., **50**, 989 (1928).

[6] Knobel, M., International Critical Tables, VI, 340.

The chloride-hypochlorite couple. From the hydrolysis of chlorine[7] and the free energy of water and chloride, one calculates the free energy of hypochlorous acid to be −19,110 cal. Using the dissociation constant for the acid by Skrabal and Berger,[8]

$$HClO = H^+ + ClO^-, \qquad K = 5.6 \times 10^{-8},$$

the free energy of formation of hypochlorite ion is −9200 cal. These values are in approximate agreement with the thermal data but lead to a value for the entropy of hypochlorite, 10 cal. per degree, which seems a little low. This would indicate that the value chosen by Bichowsky and Rossini, −29,800 for the heat formation of hypochlorous acid, may be too large negatively. The above free energies give,

$$H_2O + Cl^- = HClO + H^+ + 2e^-, \quad E^\circ = -1.49$$

$$2OH^- + Cl^- = ClO^- + H_2O + 2e^-, \quad E^\circ_B = -0.94.$$

The couple in acid solution, of course, has no chemical significance, since chloride and hypochlorous react to give chlorine.

$$Cl^- + HClO + H^+ = Cl_2 + H_2O, \qquad \Delta F^\circ = -6315 \text{ cal.}$$

The oxide, Cl_2O, is the anhydride of hypochlorous acid, and the reaction with water is reversible. Yost and Felt[9] report,

$$2HClO = Cl_2O(g) + H_2O, \qquad K = 3.54 \times 10^{-3}.$$

The chloride-chlorite couple. There are no potential or free energy data on chlorous acid; but since the entropy values are known, we may calculate the free energy from the heat of formation. Using the heat of formation of chlorous acid (−13,800 cal.), the heat of dissociation and free energy of dissociation of the acid (−4100 cal. and 2700 cal., respectively[10]), and the entropy of formation of ClO_2^- ($\Delta S° = -67$ cal. per degree), one obtains the free energy of $HClO_2$ (−600 cal.) and ClO_2^- (2100 cal.). These values then give,

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[7] Cf. International Critical Tables, VII, 233.

[8] Skrabal, A., and Berger, A., Monatsh., **70**, 168 (1937).

[9] Yost, D. M., and Felt, R. C., J. Am. Chem. Soc., **56**, 68 (1934).

[10] Barnett, B. (Ph.D. Thesis, University of California, 1935).

$$HClO_2 = H^+ + ClO_2^-, \qquad K = 10^{-2}$$

$$2H_2O + Cl^- = HClO_2 + 3H^+ + 4e^-, \qquad E° = -1.56$$

$$4OH^- + Cl^- = ClO_2^- + 2H_2O + 4e^-, \qquad E°_B = -0.76.$$

Here, also, equilibrium cannot be obtained for the couple in acid solution since chlorous acid is a strong enough oxidizing agent to oxidize chloride to chlorine. Additional couples involving chlorous acid and chloride are given in Table 11.

The chloride-chlorine dioxide couple. The heat of formation of chlorine dioxide gas, 23,500 cal., which was chosen by Bichowsky and Rossini from the work of Booth and Bowen,[11] appears quite reliable. Taking the $\Delta S°$ of formation as −17.1 cal. per degree, this gives for the free energy of formation, 28,600, and for the chloride-chlorine dioxide couple in acid and alkaline solutions,

$$2H_2O + Cl^- = ClO_2 + 4H^+ + 5e^-, \qquad E° = -1.50$$

$$4OH^- + Cl^- = ClO_2 + 2H_2O + 5e^-, \qquad E°_B = -0.84.$$

Neither of the couples can be realized in experimental equilibrium, since in acid the ClO_2 would oxidize Cl^- and in alkali the ClO_2 is unstable with respect to decomposition into chlorite and chlorate (vide infra).

The chloride-chlorate couple. Olson[12] has determined the free energy of formation of chlorate ion from equilibrium data, $\Delta F° = -250$ cal. From data by Thomsen, on two sets of reactions, Bichowsky and Rossini calculated for the heat of formation of chlorate, −24.6 and −20.8 kcal. They chose the latter value as the more probable, but an average of the two values, together with the entropy data, gives a free energy of formation which is in agreement with the work of Olson. Using this value,

$$3H_2O + Cl^- = ClO_3^- + 6H^+ + 6e^-, \qquad E° = -1.45$$

$$6OH^- + Cl^- = ClO_3^- + 3H_2O + 6e^-, \qquad E°_B = -0.62$$

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[11] Booth, H., and Bowen, E. J., J. Chem. Soc., **127**, 342 (1925).

[12] Olson, A. R., J. Am. Chem. Soc., **42**, 896 (1920).

Thus, like hypochlorous and chlorous acids, chloric acid will oxidize chloride to chlorine. The reaction is slow, however; even boiling a solution of chlorate in excess of hydrochloric acid requires some time for the complete reduction. A hot acid solution is reduced fairly rapidly by ferrous ion. Chlorate is not readily reduced at a cathode upon electrolysis of chlorate solutions.

The chloride-perchlorate couple. There are no equilibrium data on perchloric acid. However, its free energy of formation may be calculated from thermal data. Using $\Delta H^\circ = -39{,}500$ cal., and the entropy of formation $\Delta S^\circ = -96.7$ cal. per degree, the free energy of formation is $-10{,}700$ cal. Hence,

$$4H_2O + Cl^- = ClO_4^- + 8H^+ + 8e^-, \qquad E^\circ = -1.34$$

$$8OH^- + Cl^- = ClO_4^- + 4H_2O + 8e^-, \qquad E^\circ_B = -0.51$$

The potentials of the perchlorate couples are thus lower than those for any of the other oxygen acids of chlorine. Perchloric acid is a very slow oxidizing agent in $1M$ solution, and it is not reduced by boiling hydrochloric acid or by ferrous ion. Like sulfuric acid, it has a high heat of dilution and in concentrated solutions it becomes a rapid and powerful oxidizing agent.

Perchlorate radical. From the work of Gomberg[13] silver perchlorate treated with bromine yields free perchlorate, ClO_4, in which one of the oxygens has doubtless lost an electron.

The bromide couple (cf. p. 53) in the presence of silver ion would have a potential of about -2 volts, *i.e.*, it would be about 0.9 volts more negative than the E° bromine value because of the slight solubility of silver bromide. Hence the potential of the perchlorate radical must be more positive than -2 volts.

Additional chlorine half-reactions. From the half-reactions listed above, potentials may be calculated for any change of oxidation state of chlorine. For convenience, a number of these half-reaction potentials are given in Table 11.

Notes on the chlorine potentials. It will be observed in Table 11, (a), that there is a decrease in potential from HClO to ClO_4^- and likewise in (b) that the potentials for the reductions to the next lower state show the same trend. The latter fact is significant in the interpretation of the slowness of chlorate and perchlorate as oxidizing agents, as the lower potentials for the first step of the reduction act as a barrier to the net reaction.

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[13] Gomberg, M., J. Am. Chem. Soc., **45**, 398 (1923).

The following reactions, in which one oxidation state is unstable with respect to higher and lower states, are important:

$$Cl_2 + 2OH^- = Cl^- + ClO^- + H_2O, \qquad \Delta F^\circ = -19.4 \text{ kcal.}$$

$$3ClO^- = ClO_3^- + 2Cl^-, \qquad \Delta F^\circ = -43.5 \text{ kcal.}$$

$$4ClO_3^- = 3ClO_4^- + Cl^-, \qquad \Delta F^\circ = -53.5 \text{ kcal.}$$

$$2ClO_2 + 2OH^- = ClO_2^- + ClO_3^- + H_2O, \qquad \Delta F^\circ = -36.9 \text{ kcal.}$$

TABLE 11

ADDITIONAL CHLORINE HALF-REACTIONS

(a) Reduction to Cl_2 in acid solution:	E°
$\frac{1}{2}Cl_2 + 4H_2O = 8H^+ + ClO_4^- + 7e^-$	−1.34
$\frac{1}{2}Cl_2 + 3H_2O = 6H^+ + ClO_3^- + 5e^-$	−1.47
$\frac{1}{2}Cl_2 + 2H_2O = 4H^+ + ClO_2 + 4e^-$	−1.53
$\frac{1}{2}Cl_2 + 2H_2O = 3H^+ + HClO_2 + 3e^-$	−1.63
$\frac{1}{2}Cl_2 + H_2O = H^+ + HClO + e^-$	−1.63
(b) Reduction in steps in acid solution:	E°
$ClO_3^- + H_2O = 2H^+ + ClO_4^- + 2e^-$	−1.00
$ClO_2 + H_2O = 2H^+ + ClO_3^- + e^-$	−1.21
$HClO_2 + H_2O = 3H^+ + ClO_3^- + 2e^-$	−1.23
$HClO_2 = H^+ + ClO_2 + e^-$	−1.26
$HClO + H_2O = 2H^+ + HClO_2 + 2e^-$	−1.63
$\frac{1}{2}Cl_2 + H_2O = H^+ + HClO + e^-$	−1.63
$Cl^- = \frac{1}{2}Cl_2 + e^-$	−1.3583
(c) Reduction in steps in basic solution:	E°_B
$2OH^- + ClO_3^- = ClO_4^- + H_2O + 2e^-$	−0.17
$2OH^- + ClO_2 = ClO_3^- + H_2O + e^-$	0.45
$2OH^- + ClO_2^- = ClO_3^- + H_2O + 2e^-$	−0.35
$ClO_2^- = ClO_2 + e^-$	−1.15
$2OH^- + ClO^- = ClO_2^- + H_2O + 2e^-$	−0.59
$2OH^- + \frac{1}{2}Cl_2 = ClO^- + H_2O + e^-$	−0.52

The first of these is the hydrolysis of chlorine, which is practically complete in alkaline solution, but which is reversed to a measurable equilibrium in acid solution. The preparation of chloride of lime and the release of chlorine by it when acidified is an example of this equilibrium.

The second reaction is important in the commercial preparation of chlorates. If hypochlorite is heated in the presence of a catalyst, such as cobalt hydroxide, oxygen is evolved. In the absence of a catalyst, chlorate is formed and the rate of the reaction is favored by the presence of both HClO and ClO^-, that is, the reaction is slow in high concentrations of both acid and base. The reaction is not reversible.

The third reaction, the decomposition of chlorate to chloride and perchlorate, occurs if solid alkali chlorate is heated carefully in the absence of a catalyst for the decomposition into oxygen and chloride.

The last reaction goes readily in alkaline solution and the free energy would indicate that it should be reversed to give appreciable concentrations of chlorine dioxide in acid, but experimentally chlorine dioxide is not formed under these conditions.

The oxidation of chlorate to perchlorate requires a potential of only about a volt, but experimentally the most powerful oxidizing agents are required to bring it about. It may however be accomplished by anodic oxidation of alkali chlorates. The most favorable conditions are low temperature, neutral or slightly acid solution, and a smooth platinum electrode. In alkaline solution and on platinized platinum, oxygen is evolved, and the efficiency of the process is low. The oxidation is thus favored by the conditions for high oxygen overvoltage, but the influence of hydroxide upon the rate cannot be explained by reasoning based upon equilibrium data, as the potential of oxygen and perchlorate are equally dependent upon hydrogen ion. It seems likely then that the rate-determining step is the oxidation of chlorate to free ClO_3, which would be independent of hydrogen ion and cannot occur in alkaline solution where the potential is more favorable for the oxidation of water. See oxygen potential in alkali.

Bromine

The standard state of the element is the liquid, Br_2. Bichowsky and Rossini calculate for the heat of formation of the monatomic gas, $\Delta H^\circ = 26.88$ kcal. Using ΔS° for the reaction as 23.4 cal. per degree, the free energy of the monatomic gas is 19.9 kcal. Randall[14] calculates the following free energies: $Br_2(aq)$, 977 cal.; $Br_2(g)$, 755 cal.; and $Br_2(s)$, 314 cal.

Oxidation states. Bromine has compounds with the following oxidation numbers: −1, hydrobromic acid and its salts; +1, hypobromous acid; and +5, bromic acid and the bromates. Bromous acid, +3, is doubtless formed as an intermediate step in various reactions, but it is too unstable to exist in appreciable concentrations. Perbromic acid or its salts, +7, are unknown. Evidence has recently been presented of the oxides Br_2O and BrO_2.[15]

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[14] International Critical Tables, VII, 234.

The bromide-bromine couple. From cell measurements by Jones and Baeckström,[16]

$$2Br^- = Br_2(l) + 2e^-, \qquad E^\circ = -1.0652$$

$$2Br^- = Br_2(aq) + 2e^-, \qquad E^\circ = -1.087.$$

The corresponding free energy of bromide ion, Br^-, is −24,578 cal.

From the heat of formation, −28,670 cal., given by Bichowsky and Rossini, and the entropy of formation, −14.3 cal. per degree, the free energy is −24,410 cal. in fair agreement with the cell measurements.

The couple is reversible and bromine is a comparatively rapid oxidizing agent. The overvoltage for the anodic oxidation of bromide is given by Knobel[17] as somewhat less than the values for chlorine.

At a concentration of $10^{-7}M$ H^+, bromine has a potential of 0.2 volts in favor of the oxidation of water, but the reaction is reversed in one molal acid. However, in low acid the reaction is not rapid, and bromine solutions in water are comparatively stable.

Bromine reacts with bromide to form the tribromide Br_3^-. From the work of Griffith, McKeown, and Winn,[18]

$$Br_2(aq) + Br^- = Br_3^-, \qquad K = 17.$$

Hence the free energy of formation of Br_3^- is −25,270 cal. and

$$3Br^- = Br_3^- + 2e^-, \qquad E^\circ = -1.05.$$

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[15] Brenschede, W., and Schumacher, H. J., Z. anorg. allgem. Chem., **226,** 370 (1936); Schwarz, R., and Schmeisser, M., Ber., **70 B,** 1163 (1937).

[16] Jones, G., and Baeckström, S., J. Am. Chem Soc., **56,** 1524 (1934); cf. also Randall, M., International Critical Tables, **VII,** 234.

[17] Knobel, M., International Critical Tables, **VI,** 340.

[18] Griffith, R. O., McKeown, A., and Winn, A. G., Trans. Faraday Soc., **28,** 101 (1932).

At high concentration the pentabromide appears to form, and Liebhafsky[19] calculates the constant for the dissociation of Br_5^- to be 0.055.

The bromide-hypobromite couple. Liebhafsky[20] has reviewed the data on the hydrolysis of bromine and gives $K = 5.8 \times 10^{-9}$ as the best value. This leads to $-19{,}900$ cal. as the free energy of formation of HBrO. Shilov[21] reported,

$$HBrO = H^+ + BrO^-, \qquad K = 2.06 \times 10^{-9}.$$

One then calculates -8000 cal. as the free energy of BrO^-. These values appear to be consistent with the heat of formation of hypobromous acid, $\Delta H° = -25{,}200$ cal. given by Bichowsky and Rossini. For the bromide-hypobromite couple one calculates:

$$H_2O + Br^- = HBrO + H^+ + 2e^-, \qquad E° = -1.33$$

$$2OH^- + Br^- = BrO^- + H_2O + 2e^-, \qquad E°_B = -0.76.$$

Hypobromous acid cannot be prepared except at the very low concentrations given by the hydrolysis of bromine; and when alkali is added, the hypobromite ion decomposes almost instantly into bromide and bromate.

The bromide-bromate couple. Lewis and Randall calculate from the measurements of Sammet[22] on the bromine-bromate electrode that the free energy of formation of BrO_3^- is 2300 cal. The third law value, calculated from the heat of formation ($-11{,}200$ cal.) given by Bichowsky and Rossini, and the entropy of formation (47.0 cal. per degree), is 9700 cal. High accuracy cannot be claimed for either the heat of formation or the cell measurements. The value $\Delta F° = 5000$ cal. will be chosen, and also the same value will be used for $HBrO_3$, since it is a strong acid. Then,

$$3H_2O + Br^- = BrO_3^- + 6H^+ + 6e^-, \qquad E° = -1.44$$

$$6OH^- + Br^- = BrO_3^- + 3H_2O + 6e^-, \qquad E° = -0.61.$$

Equilibrium for the couple in acid would be impossible, since bromate will oxidize bromide to bromine. Bromic acid is a more rapid oxidizing agent than chloric acid, and in high acid it will oxidize water to oxygen.

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[19] Liebhafsky, H. A., J. Am. Chem. Soc., **56**, 1500 (1934).
[20] Liebhafsky, *ibid.*
[21] Shilov, E. A., J. Am. Chem. Soc., **60**, 490 (1938).
[22] Sammet, V., Z. physik. Chem., **53**, 678 (1905).

Bromine chloride as an oxidizing agent. The spectroscopic data for the entropy and heat of formation of bromine chloride appear to be very good. Using the value of Jost[23] for the heat of formation, 3070 cal., and the entropy of formation, 12.1 cal. per degree, one obtains −530 cal. as the free energy of formation of BrCl.

$$Br^- + Cl^- = BrCl(g) + 2e^-, \qquad E^\circ = -1.20.$$

Additional bromine half-reactions. From the half-reactions listed above, potentials may be calculated for any reaction involving a change in the oxidation state of bromine. For convenience, a number of these potentials are given in Table 12.

TABLE 12

ADDITIONAL BROMINE HALF-REACTIONS

(*a*) **Reduction to Br_2 in acid solution:**	E°
$\frac{1}{2}Br_2 + 3H_2O = BrO_3^- + 6H^+ + 5e^-$	−1.52
$\frac{1}{2}Br_2 + H_2O = HBrO + H^+ + e^-$	−1.59
(*b*) **Reduction in steps in acid solution:**	E°
$2H_2O + HBrO = BrO_3^- + 5H^+ + 4e^-$	−1.49
$H_2O + \frac{1}{2}Br_2 = HBrO + H^+ + e^-$	−1.59
$Br^- = \frac{1}{2}Br_2 + e^-$	−1.066
(*c*) **Reduction in steps in alkaline solution:**	E°
$4OH^- + BrO^- = BrO_3^- + 2H_2O + 4e^-$	−0.54
$2OH^- + \frac{1}{2}Br_2 = BrO^- + H_2O + e^-$	−0.45

Notes on the bromine potentials. The free energy of the simultaneous oxidation-reduction of bromine in alkaline solutions may be calculated from the potentials above.

$$3Br_2 + 6OH^- = 5Br^- + BrO_3^- + 3H_2O, \qquad \Delta F^\circ = -62{,}400 \text{ cal.}$$

This reaction goes readily in alkali, but in acid solution it is reversed, as indicated by the free energy.

$$5Br^- + BrO_3^- + 6H^+ = 3Br_2 + 3H_2O, \qquad \Delta F^\circ = -52{,}200 \text{ cal.}$$

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[23] Jost, W., Z. physik. Chem., **A 153**, 143 (1931).

The first step of the bromine in alkali reaction is doubtless the hydrolysis reaction,

$$Br_2 + 2OH^- = BrO^- + Br^- + H_2O, \qquad \Delta F^\circ = -14{,}100 \text{ cal.},$$

followed by the rapid oxidation-reduction of the hypobromite

$$3BrO^- = 2Br^- + BrO_3^-, \qquad \Delta F^\circ = -30{,}900 \text{ cal.}$$

Iodine

The standard state of the element is the solid I_2. The free energy of the monatomic gas may be calculated from the heat of formation by Bichowsky and Rossini, 25.59 kcal., and the entropy of formation, 29.24 cal. per degree. This value is 16.87 kcal. The International Critical Tables[24] give the following free energies, based upon the calculations of Lewis and Randall: $I_2(g)$, $\Delta F^\circ = 4630$ cal. and $I_2(aq)$, $\Delta F^\circ = 3926$ cal.

Oxidation states. Iodine has an oxidation number of −1 in hydroiodic acid and its salts, +1 in the unstable hypoiodous acid and iodine monochloride, +5 in iodic acid and its salts, and +7 in periodic acids and its derivatives. The +4 oxide, IO_2 or I_2O_4, has been prepared. There is also some evidence for I_2O_3. It seems probable that HIO_2 (oxidation number +3) is formed momentarily in the oxidation of iodine or the reduction of iodate, and the trichloride ICl_3, in which the iodine may be considered as +3, is well known.

The iodide-iodine couple. From the iodide-iodine electrode and accurate measurements of the activity of iodide solutions, Randall[25] calculated the free energy of iodide, I^-, to be −12,333 cal. and the half-reaction,

$$2I^- = I_2 + 2e^-, \qquad E^\circ = -0.5345.$$

The value of the free energy of iodide from the heat and entropy of formation is −12,190 cal.

Although, as the potential value indicates, iodine is not a powerful oxidizing agent, its action is in general rapid, that is, the heat of activation is small. However, Knobel[26] gives the overvoltage for the liberation of iodine on platinum as higher than the corresponding values for bromine or chlorine. This is difficult to understand in view of the lower energy of dissociation of the I_2 molecule.

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[24] International Critical Tables, VII, 235.

[25] Randall, M., *op. cit.* Cf. also Bates, R. G., and Vosburgh, W. C., J. Am. Chem. Soc., **59**, 1190 (1937).

The iodide-triiodide couple. Lewis and Randall[27] have reviewed the data on the free energy of the reaction, iodine and iodide to give triiodide, I_3^-. Using their value and the iodide free energy above, one obtains for the free energy of triiodide $-12{,}290$ cal.

$$I_2(aq) + I^- = I_3^-, \qquad K = 1.4 \times 10^{-3}$$

$$3I^- = I_3^- + 2e^-, \qquad E^\circ = -0.5355$$

The iodide-hypoiodite couple. From the work of Bray and Connolly[28] on the hydrolysis of iodine, the free energy of formation of hypoiodous acid is $-23{,}330$ cal. Then for the couple,

$$H_2O + I^- = HIO + H^+ + 2e^-, \qquad E^\circ = -0.99.$$

Fürth[29] gave as a rough value for the dissociation constant of hypoiodous acid, $K = 10^{-11}$. This would make the free energy of the hypoiodite ion -8300 cal.

$$2OH^- + I^- = IO^- + H_2O + 2e^-, \qquad E_B^\circ = -0.49.$$

The agreement with the thermal data is not very good, but the equilibrium data are probably to be preferred, although no high accuracy can be claimed for them, since these substances are too unstable to permit any direct calorimetric determinations. The energies of these decomposition reactions will be discussed in a later paragraph.

Iodine monochloride. Hypoiodous acid has basic properties, and in moderately large concentration of hydrochloric acid it forms ICl and ICl_2^-. Faull[30] has determined the equilibrium constants for the reactions,

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[26] Knobel, M., International Critical Tables, *op. cit.*

[27] Lewis, G. N., and Randall, M., *Thermodynamics* (McGraw-Hill, New York, 1923), p. 526. Cf. also Jones, G., and Kaplan, B. B., J. Am. Chem. Soc., **50,** 1845 (1928).

[28] Bray, W. C., and Connolly, E. L., J. Am. Chem. Soc., **33,** 1485 (1911).

[29] Fürth, A., Z. Electrochem., **28,** 57 (1922).

$$ICl_2^- = ICl(aq) + Cl^- \qquad K = 6 \times 10^{-3}$$

$$2ICl(aq) = I_2(aq) + Cl_2(aq), \qquad K = 1.6 \times 10^{-10}.$$

These constants lead to the values of the free energy of formation of ICl(aq), −4000 cal., and of ICl_2^-, −38,350 cal. The thermal data seem to indicate that these figures are too large negatively, but Faull's values are doubtless the more reliable. The work of Philbrick[31] also is in substantial agreement. The most important potentials are the reduction to iodine and chloride.

$$Cl^- + \tfrac{1}{2}I_2 = ICl(aq) + e^-, \qquad E^\circ = -1.19$$

$$2Cl^- + \tfrac{1}{2}I_2 = ICl_2^- + e^-, \qquad E^\circ = -1.06.$$

Iodine monobromide. Faull has also determined the corresponding constants for IBr_2^- and IBr and finds

$$IBr_2^- = IBr(aq) + Br^-, \qquad K = 2.7 \times 10^{-3}$$

$$2IBr(aq) = I_2(aq) + Br_2(aq), \qquad K = 1.2 \times 10^{-5}.$$

The free energies are IBr(aq), −900 cal., and IBr_2^-, −28,970 cal.; and the potentials to iodine and bromide are:

$$Br^- + \tfrac{1}{2}I_2 = IBr(aq) + e^-, \qquad E^\circ = -1.02$$

$$2Br^- + \tfrac{1}{2}I_2 = IBr_2^- + e^-, \qquad E^\circ = -0.87$$

Iodine trichloride. Nies and Yost[32] give −21,150 cal. as the free energy of formation of the trichloride ICl_3. Hence,

$$2Cl^- + ICl(s) = ICl_3(s) + 2e^-, \qquad E^\circ = -0.99$$

$$3Cl^- + \tfrac{1}{2}I_2 = ICl_3(s) + 3e^-, \qquad E^\circ = -1.05.$$

The iodide-iodate couple. Lundberg, Vestling, and Ahlberg[33] found −32,251 cal. for the free energy of formation of iodate,

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[30] Faull, J. H., J. Am. Chem. Soc., **56**, 522 (1934).

[31] Philbrick, F. A., J. Am. Chem. Soc., **56**, 1257 (1934).

[32] Nies, N. P., and Yost, D. M., J. Am. Chem. Soc., **57**, 306 (1935).

[33] Lundberg, W. O., Vestling, C. S., and Ahlberg, J. E., J. Am. Chem. Soc., **59**, 264 (1937).

IO_3^-, which is in agreement with the thermal data. This gives for the iodide-iodate couples,

$$3H_2O + I^- = IO_3^- + 6H^+ + 6e^-, \qquad E^\circ = -1.085$$

$$6OH^- + I^- = IO_3^- + 3H_2O + 6e^-, \qquad E^\circ_B = -0.26.$$

Iodate in acid solution is a rapid oxidizing agent and oxidizes iodide to iodine. This reaction may be used to determine I^-, IO_3^-, or H^+, quantitatively. With the iodine-iodate couple, reversible equilibria may be attained. The free energy of the iodate ion used in these calculations was derived from direct measurements of this electrode (cf. also Table 13, p. 60).

Periodic acid. Of the various hypothetical hydrates of iodine heptoxide, the following are the more important: paraperiodic acid, H_5IO_6; metaperiodic acid, HIO_4; and mesodiperiodic acid, $H_4I_2O_9$. The paraperiodic acid is the only solid acid which exists in equilibrium with water. The solubility is quite high. The composition of the solution is probably largely this acid, although slightly soluble meta-salts, for example, KIO_4, may be precipitated upon the addition of the metal ion to the acid solution. The acid is not very strong.[34]

$$H_5IO_6 = H^+ + H_4IO_6^-, \qquad K = 2.3 \times 10^{-2}$$

$$H_4IO_6^- = H^+ + H_3IO_6^{--}, \qquad K = \text{ca } 10^{-6}.$$

The second dissociation is complicated by the formation of the mesodiperiodate,

$$2H_3IO_6^{--} = I_2O_9^{----} + 3H_2O,$$

and salts corresponding to both of these ions may exist in equilibrium with the solution, for example, $Na_2H_3IO_6$, and $K_4I_2O_9 \cdot 9H_2O$. The addition of more alkali to the solid sodium salt converts it to $Na_3H_2IO_6$; and in the case of the very slightly soluble silver salts, all the hydrogens of the para-acid appear to be replaceable, for example, Ag_5IO_6. However, the third ionization constant must be quite small, and there is no evidence for the formation of appreciable concentrations of the ion $H_2IO_6^{---}$ in 1 M KOH.

Abel and Smetana[35] studied the potential of the iodate-periodate couple and gave for the E° in acid solution -1.51. However, they considered the periodic acid to be completely dissociated and to have the formula HIO_4. In view of the fact that periodic acid will quantitatively oxidize manganous ion to permanganate, $E^\circ = -1.52$, their value appears to be too low. The heat of formation data are somewhat conflicting and there are no data on the entropy of periodic acid. From purely chemical evidence we shall write,

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[34] Rae, N., J. Chem. Soc., p. 876 (1931).

[35] Abel, E., and Smetana, O., Monatsh., **60**, 181 (1932).

$$3H_2O + IO_3^- = H_5IO_6 + H^+ + 2e^-, \qquad E^\circ = \text{ca } -1.7.$$

The corresponding free energy of formation of periodic acid is ca −123,900 cal. For the couple in alkaline solution, one computes from the approximate ionization constants given above,

$$3OH^- + IO_3^- = H_3IO_6^{--} + 2e^-, \qquad E_B^\circ = \text{ca } -0.7.$$

The iodate-periodate couple, even in neutral or slightly alkaline solution, will oxidize iodide to iodine. This is a distinction from iodate.

TABLE 13

ADDITIONAL IODINE HALF-REACTIONS

(a) **Reduction to iodine in acid solution:**	E°
$\frac{1}{2}I_2 + 6H_2O = H_5IO_6 + 7H^+ + 7e^-$	ca -1.35
$\frac{1}{2}I_2 + 3H_2O = IO_3^- + 6H^+ + 5e^-$	-1.195
$\frac{1}{2}I_2 + H_2O = HIO + H^+ + e^-$	-1.45
(b) **Reduction in steps in acid solution:**	E°
$3H_2O + IO_3^- = H_5IO_6 + H^+ + 2e^-$	ca -1.70
$2H_2O + HIO = IO_3^- + 5H^+ + 4e^-$	-1.13
$3H_2O + ICl_2^- = IO_3^- + 6H^+ + 2Cl^- + 4e^-$	-1.23
$2Cl^- + \frac{1}{2}I_2 = ICl_2^- + e^-$	-1.06
$2I^- = I_2 + 2e^-$	-0.5345
(c) **Reduction in steps in alkaline solution:**	E_B°
$3OH^- + IO_3^- = H_3IO_6^{--} + 2e^-$	ca -0.70
$4OH^- + IO^- = IO_3^- + 2H_2O + 4e^-$	-0.56
$2OH^- + I^- = IO^- + H_2O + 2e^-$	-0.49

Periodates may be made from iodates by anodic oxidation on a smooth platinum anode. The most favorable conditions are low temperature and high concentrations of iodate and hydroxide.

Additional iodine half-reactions. The couples in Table 13 may be derived from equations given above, and have been listed for convenience.

Notes on the iodine couples. A number of important relations between the iodine oxidation states may be discussed in terms of these potential values.

Unlike chlorate, iodate is not unstable with respect to decomposition into higher and lower states.

$$9H_2O + 7IO_3^- + 7H^+ = I_2 + 5H_5IO_6 \qquad \Delta F^\circ = 116 \text{ kcal.}$$

$$3H_2O + 3OH^- + 4IO_3^- = I^- + 3H_3IO_6^{--}, \quad \Delta F^\circ = 60 \text{ kcal.}$$

As these positive free energies indicate, the reverse reactions, in both acid and base, go readily.

Hypoiodous acid and hypoiodite in alkali are unstable with respect to their own oxidation and reduction.

$$5HIO = 2I_2 + IO_3^- + H^+ + 2H_2O, \qquad \Delta F^\circ = -29.0 \text{ kcal.}$$

$$3IO^- = 2I^- + IO_3^-, \qquad \Delta F^\circ = -32 \text{ kcal.}$$

Since the iodous acid, HIO_2, which is postulated as an intermediate step in many reactions, does not exist in appreciable concentrations, it is unstable with respect to the reaction,

$$5HIO_2 = I_2 + 3IO_3^- + 3H^+ + H_2O.$$

From the free energies of the other substances involved, ΔF° for HIO_2 must be $> -30{,}000$ cal. and

$$2H_2O + \tfrac{1}{2}I_2 = HIO_2 + 3H^+ + 3e^-,$$
$$E^\circ < -1.2.$$

The oxidation of iodine to ICl_2^- by iodate in hydrochloric acid is a well-known analytical procedure. From the potentials we may calculate

$$IO_3^- + 6H^+ + 10Cl^- + 2I_2 = 5ICl_2^- + 3H_2O,$$
$$\Delta F^\circ = -16.3 \text{ kcal.}$$

The small value for the free energy is in agreement with the fact that a moderately high concentration of hydrochloric acid is required to make the reaction quantitative.

Notes on the potentials of the halogen group. Table 14 has been given to provide a comparison of some of the more important couples of the halogen group.

TABLE 14

COMPARISON OF HALOGEN COUPLES

Acid Solution

$$\begin{tikzcd}
F^- \arrow[r, dash, "-2.85"] & F_2
\end{tikzcd}$$

$$\begin{tikzcd}
Cl^- \arrow[r, dash, "-1.36"] & Cl_2 \arrow[r, dash, "-1.63"] \arrow[rrr, dash, bend right, "-1.47"'] & HClO \arrow[r, dash, "-1.63"] & HClO_2 \arrow[r, dash, "-1.23"] & ClO_3^- \arrow[r, dash, "-1.00"] & ClO_4^-
\end{tikzcd}$$

$$\begin{tikzcd}
Br^- \arrow[r, dash, "-1.07"] & Br_2 \arrow[r, dash, "-1.59"] \arrow[rr, dash, bend right, "-1.52"'] & HBrO \arrow[r, dash, "-1.49"] & BrO_3^-
\end{tikzcd}$$

$$\begin{tikzcd}
I^- \arrow[r, dash, "-0.53"] & I_2 \arrow[r, dash, "-1.45"] \arrow[rr, dash, bend right, "-1.20"'] & HIO \arrow[r, dash, "-1.14"] & IO_3^- \arrow[r, dash, "\text{ca } -1.70"] & H_5IO_6
\end{tikzcd}$$

Basic Solution

$$\begin{tikzcd}
F^- \arrow[r, dash, "-2.85"] & F_2
\end{tikzcd}$$

$$\begin{tikzcd}
Cl^- \arrow[r, dash, "-1.36"] \arrow[rr, dash, bend right, "-0.94"'] & Cl_2 \arrow[r, dash, "-0.52"] & ClO^- \arrow[r, dash, "-0.59"] & ClO_2^- \arrow[r, dash, "-0.35"] & ClO_3^- \arrow[r, dash, "-0.17"] & ClO_4^-
\end{tikzcd}$$

$$\begin{tikzcd}
Br^- \arrow[r, dash, "-1.07"] \arrow[rr, dash, bend right, "-0.76"'] & Br_2 \arrow[r, dash, "-0.45"] & BrO^- \arrow[r, dash, "-0.54"] & BrO_3^-
\end{tikzcd}$$

$$\begin{tikzcd}
I^- \arrow[r, dash, "-0.53"] \arrow[rr, dash, bend right, "-0.49"'] & I_2 \arrow[r, dash, "-0.45"] & IO^- \arrow[r, dash, "-0.56"] & IO_3^- \arrow[r, dash, "\text{ca } -0.7"] & H_3IO_6^{--}
\end{tikzcd}$$

The marked decrease in the oxidizing power of the free halogen from fluorine to iodine is to be noted. This leads to the replacement of a heavier halide by a lighter. For example,

$$Cl_2 + 2Br^- = Br_2 + 2Cl^-.$$

A number of other so-called replacements occur with the oxygen ions, such as

$$BrO_3^- + I^- = IO_3^- + Br^-,$$

but these, of course, are complicated reactions occurring in steps and are not simple replacements.

Most of these potentials are more negative than the water-oxygen couple, -1.23, and are capable, therefore, of liberating oxygen from water. With the exception of fluorine, these reactions, however, are slow.

The most powerful oxidizing couple among the oxygen ions is the periodate-iodate, but in alkaline solution the potential falls to a value somewhat less than the chloride-hypochlorite couple (cf. Table 11, p. 51); hence hypochlorite will partially oxidize iodate, and if silver ion is present, the equilibrium may be displaced to give practically complete oxidation of the iodate to periodate.

CHAPTER VI

Sulfur, Selenium, Tellurium, and Polonium

Oxygen, the first member of Group VI, has been discussed in Chapter IV. Like oxygen, the other members of the group show a tendency to complete the octet of $s-p$ electrons by the addition of two electrons, but the stability of the -2 oxidation state decreases with increasing atomic weight. With the lighter elements, the $+4$ and $+6$ states are the most stable, but the compounds of the latter increase in oxidizing power with the heavier elements and probably do not exist with polonium. The $+2$ state is unstable with respect to the decomposition into the element and the $+4$ state, except in the case of polonium. Odd oxidation numbers are impossible with completed octets except by sharing a pair of electrons between two atoms of the group, for example, NaS_2, and are generally unstable with respect to the even states.

Sulfur

The standard state of the element is solid rhombic sulfur. Randall[1] gives the following free energies: S (monoclinic, solid), 18.3 cal.; and S (l), 94 cal. From the Bichowsky and Rossini heats of formation and the entropies, the following free energies may be calculated: $S_2(g)$, 17,500 cal.; S(g), 56,600 cal.; $S_6(g)$, 8800 cal.; and $S_8(g)$, 5700 cal.

Oxidation states. Sulfur has an oxidation number of -2 in sulfides. It forms polysulfides, for example, S_3^{--}, in which the average sulfur oxidation number is negative; but in these compounds it is rather ambiguous to assign polar numbers, as the sulfur atoms are linked by covalent bonds. The monoxide SO, with oxidation number of $+2$, is known as an unstable gas molecule, and derivatives of the acid H_2SO_2, the sulfoxylates, exist. The average oxidation number of $+2$ also occurs in the thiosulfates and pentathionates. Hyposulfite, $S_2O_4^{--}$, corresponds to a value of +3 for the oxidation number, and sulfite, SO_3^{--}, is +4. The +5 state is represented by dithionate, and the sulfates are +6. The so-called persulfates are peroxy-compounds. Numerous compounds are known in which the average oxidation number is a positive fraction, as in $S_3O_6^{--}$ and $S_4O_6^{--}$. The problem of assigning oxidation states in these compounds is similar to that of the polysulfides mentioned above. Compounds with the halogens are known in which the sulfur has oxidation states of +1, +2, +4, and +6.

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[1] International Critical Tables, VII, 236.

The sulfide-sulfur couple. From the heat of formation of hydrogen sulfide by Zeumer and Roth[2] (−4800 cal.) and the entropy of formation (10.3 cal. per degree), the free energy of formation of $H_2S(g)$ is −7870 cal. Combining this with the Lewis and Randall values for the free energies of solution and dissociation, one obtains: $H_2S(aq)$, −6520 cal.; HS^-, 2950 cal.; and S^{--}, 23,420 cal.

$$H_2S = H^+ + HS^-, \qquad K = 1.15 \times 10^{-7}$$

$$HS^- = H^+ + S^{--}, \qquad K = 1.0 \times 10^{-15}$$

The half-reaction potentials then are,

$$H_2S = S + 2H^+ + 2e^-, \qquad E^\circ = -0.141$$

$$S^{--} = S + 2e^-, \qquad E_B^\circ = 0.508$$

$$OH^- + HS^- = S + H_2O + 2e^-, \qquad E_B^\circ = 0.479$$

Since a $1M$ NaS_2 solution contains 90 per cent HS^-, the latter couple would correspond more nearly to the net reaction in $1M$ OH^-. However, as sulfur dissolves in sulfide to form polysulfide, this couple could not be attained in equilibrium. Because of its slowness, the acid couple is not thermodynamically reversible. Hydrogen sulfide is oxidized rapidly and quantitatively to sulfur by iodine and ferric ion. More powerful oxidizing agents, such as bromine, will take the sulfur on to sulfate.

The polysulfides. The free energy and heat of formation of S^{--} lead to a value of −6 cal. per degree for the entropy of S^{--}. Using the Bichowsky and Rossini values for the heats of formation and assuming the entropies S_2^{--}, 0; S_3^{--}, +5; and S_4^{--}, +10; one calculates the free energies: S_2^{--}, 23,100 cal.; S_3^{--}, 22,400 cal.;

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[2] Zeumer, H., and Roth, W. A., Z. Elektrochem., **40**, 777 (1934).

and S_4^{--}, 20,700 cal. The potentials of the following couples are of interest:

$$2S^{--} = S_2^{--} + 2e^-, \qquad E_B^\circ = 0.51$$

$$S^{--} + S_2^{--} = S_3^{--} + 2e^-, \qquad E_B^\circ = 0.52$$

$$S^{--} + S_3^{--} = S_4^{--} + 2e^-, \qquad E_B^\circ = 0.55.$$

The hydrogen ions, for example, HS_2^{--}, are doubtless largely present in a one molal alkali solution and the heats and free energies of the reactions have not been corrected for these hydrolysis effects, as the ionization constants are not known. Except for this point the potentials are probably fairly good.

The sulfur-sulfurous acid couple. Eckman and Rossini[3] have measured the heat of formation of $SO_2(g)$, $-70{,}920$ cal. Since the entropies are well known, this should give the most accurate value for the free energy of formation. Based on ΔS° as 2.73 cal. per degree, the free energy of $SO_2(g)$ is $-71{,}735$ cal. From the Lewis and Randall free energy of solutions, ΔF° for $H_2SO_3(aq)$ is $-128{,}535$ cal. Sherrill and Noyes[4] give 0.012 for the first dissociation constant for H_2SO_3, and Kolthoff[5] gives 1×10^{-7} for the second constant. These values lead to the free energies HSO_3^-, $-125{,}905$ cal., and SO_3^{--}, $-116{,}400$ cal. Hence,

$$H_2SO_3 = H^+ + HSO_3^-, \qquad K = 1.2 \times 10^{-2}$$

$$HSO_3^- = H^+ + SO_3^{--}, \qquad K = 1 \times 10^{-7}$$

$$3H_2O + S = H_2SO_3 + 4H^+ + 4e^-, \qquad E^\circ = -0.45$$

$$6OH^- + S^{--} = SO_3^{--} + 3H_2O + 6e^-, \qquad E_B^\circ = 0.61.$$

From these potentials sulfurous acid is a fairly good oxidizing agent, while sulfite ion is very much weaker. The mechanism of the reduction probably goes through hyposulfurous acid with the one electron type of reducing agent.

The sulfite-sulfate couple. The heat of formation of sulfate ion, $-215{,}800$ cal., and the entropy of formation, -133 cal. per degree, give $-176{,}100$ cal. for the free energy of SO_4^{--}. The same value will be taken for H_2SO_4. On this basis the slight weakness of HSO_4^-, $K = 0.012$, must be included in the sulfuric acid activity.

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[3] Eckman, J. R., and Rossini, F. R., U. S. Bur. Standards J. Research, **3**, 597 (1929).

[4] Sherrill, M. S., and Noyes, A. A., J. Am. Chem. Soc., **48**, 1861 (1926).

[5] Kolthoff, I. M., Chem. Weekblad, **16**, 1154 (1919).

$$H_2O + H_2SO_3 = SO_4^{--} + 4H^+ + 2e^-, \qquad E^\circ = -0.20$$

$$2OH^- + SO_3^{--} = SO_4^{--} + H_2O + 2e^-, \qquad E_B^\circ = 0.90.$$

Sulfuric acid in molal solutions is thus a poor oxidizing agent, considerably weaker than the sulfurous acid. The heat of concentration to form pure H_2SO_4, however, is 15 kcal. Hence, the concentrated acid becomes a stronger oxidizing agent, especially when heated, as the fugacity of the SO_2 which is formed increases rapidly with temperature.

Thiosulfate and tetrathionate. Bichowsky[6] determined the equilibrium in the reaction

$$SO_3^{--} + S(r) = S_2O_3^{--}.$$

His value for the free energy of the reaction, −8430 cal., leads to −124,800 cal. for the free energy of $S_2O_3^{--}$. The accepted heat of formation of thiosulfate appears to be inconsistent with the free energy data, and a slightly lower value, −124,000 cal., will be taken arbitrarily as the free energy of thiosulfate.

$$3H_2O + S_2O_3^{--} = 2H_2SO_3 + 2H^+ + 4e^-, \qquad E^\circ = -0.40$$

$$6OH^- + S_2O_3^{--} = 2SO_3^{--} + 3H_2O + 4e^-, \qquad E_B^\circ = 0.58.$$

However, with many oxidizing agents the thiosulfate is oxidized to tetrathionate, $S_4O_6^{--}$. Thomsen[7] has measured the heat of the reaction of iodine with thiosulfate. There is considerable uncertainty in the interpretation of his value, 7950 cal. Considering his results, the probable entropy of the reaction, and other requirements which the free energy of $S_4O_6^{--}$ must meet, the free energy of the reaction is taken as,

$$2S_2O_3^{--} + I_2(s) = S_4O_6^{--} + 2I^-, \qquad \Delta F^\circ = -16{,}500 \text{ cal.}$$

and combining with the potential of the iodine couple,

$$2S_2O_3^{--} = S_4O_6^{--} + 2e^-, \qquad E^\circ = -0.17.$$

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[6] Bichowsky, F. R., J. Am. Chem. Soc., **45**, 2225 (1923).

[7] Thomsen, J., *Thermochemistry* (Longmans, New York, 1908), p. 213.

The free energy of formation of $S_4O_6^{--}$ is $-240,000$ cal. and the potential for the tetrathionate-sulfurous acid couple,

$$6H_2O + S_4O_6^{--} = 4H_2SO_3 + 4H^+ + 6e^-, \quad E^\circ = -0.48.$$

Any oxidizing agent which is capable of oxidizing tetrathionate to sulfurous acid will, of course, take the sulfurous acid on to sulfate. It is interesting to note that the above potential is about the same as the iodide-iodine couple. Since iodine will not oxidize tetrathionate, the first step in the mechanism of the $S_4O_6^{--}$ oxidation may have a potential which is more negative than the overall value.

The oxidation of thiosulfate to tetrathionate may be carried out by electrolysis of alkali sulfites, the highest efficiency being obtained at low hydrogen-ion concentration. The process always results in some sulfate formation, and the ratio of tetrathionate to sulfate varies[8] with the presence of many substances. For example, the ratio is high in the presence of cobalt sulfate and low in the presence of molybdate. The reaction mechanism is doubtless complicated, and the ratio depends upon the potentials of the intermediate sulfur compounds and their relation to those of other oxidation-reduction couples which may be present either as added catalysts or formed by oxidation of the surface of the anode. The anodic oxidation potential is far higher than the reversible potential calculated above, the overvoltage being at least one volt.

Sulfoxylic acid. Salts of sulfoxylic acid, H_2SO_2, are known, and the acid is said to be unstable with respect to the reaction,

$$2H_2SO_2 = S_2O_3^{--} + 2H^+ + H_2O.$$

From the free energies of thiosulfate and water, the free energy of sulfoxylic acid must be more positive than $-90,000$ cal. and

$$2H_2O + S = H_2SO_2 + 2H^+ + 2e^-, \qquad E^\circ < -0.5$$

$$H_2O + H_2SO_2 = H_2SO_3 + 2H^+ + 2e^-, \qquad E^\circ > -0.4$$

Hyposulfurous acid. Jellinek[9] has measured the potential for the reaction,

$$S_2O_4^{--} + 2H_2O = H_2 + 2HSO_3^-, \qquad E^\circ = 0.01.$$

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[8] Cf. Glasstone, S., and Hickling, A., J. Chem. Soc., 2345 (1932).

[9] Jellinek, K., *Das Hydrosulfit* (Enke, Stuttgart, 1911), p. 71.

This would make the free energy of $S_2O_4^{--}$, −138,000 cal. However, Berthelot[10] has measured the heat of the reaction hyposulfite with oxygen to give bisulfite; and this thermal data, with the assumption of 8 cal. per degree as the entropy of $S_2O_4^{--}$, gives −126,000 cal. for the free energy of formation. Both of these measurements were subject to large errors; hence, −130,000 cal. will be chosen as an approximate value. Hyposulfurous acid is surprisingly strong. The acid dissociation constants are given as $K_1 = 0.45$ and $K_2 = 0.0035$ by Jellinek. In view of the large value for the first ionization, it will be treated as complete. The free energy of the acid ion $HS_2O_4^-$, from the value of K_2 and the free energy chosen for hyposulfite, then, is −133,300 cal. The potentials in acid and base derived from these free energies are,

$$2H_2O + HS_2O_4^- = 2H_2SO_3 + H^+ + 2e^-, \qquad E^\circ = 0.23$$

$$4OH^- + S_2O_4^{--} = 2SO_3^{--} + 2H_2O + 2e^-, \quad E_B^\circ = 1.4.$$

Hyposulfite in alkaline solution is thus a powerful reducing agent. It is unstable with respect to the decomposition,

$$2S_2O_4^{--} + H_2O = S_2O_3^{--} + 2HSO_3^-, \quad \Delta F^\circ = -59{,}100 \text{ cal.},$$

and the rate of the decomposition is more rapid in acid solution.

Hyposulfite may be prepared by cathodic reduction of bisulfite, HSO_3^-, solution. The solution must not be too acidic or the above decomposition will occur, and it must not be too alkaline since the reduction becomes difficult, as is indicated by the high positive value for the potential in molal hydroxide. The mechanism of the reduction is unknown, but many substances appear to catalyse the formation of the hyposulfite.

The thionic acids. Bichowsky and Rossini give the following heats of reaction relating the thionic acids:

$$S_2O_6^{--} + S = S_3O_6^{--}, \qquad \Delta H^\circ = 1.2 \text{ kcal.}$$

$$S_3O_6^{--} + S = S_4O_6^{--}, \qquad \Delta H^\circ = 6.7 \text{ kcal.}$$

$$S_4O_6^{--} + S = S_5O_6^{--}, \qquad \Delta H^\circ = 2.8 \text{ kcal.}$$

Because the entropy change in these reactions is probably zero within the accuracy with which the reaction heats are known, the free energies may be taken equal to the heats. Then using the value for the free energy of tetrathionate which was obtained above, one calculates the following free energies: $S_2O_6^{--}$, −248,000 cal.; $S_3O_6^{--}$, −247,000 cal.; and $S_5O_6^{--}$, −237,000 cal. These values all appear to be somewhat too large negatively when compared with the heats of formation and the probable entropies of formation; however, it would be difficult to make the free energy of tetrathionate smaller in relation to the values which have been chosen for SO_3^{--} and $S_2O_3^{--}$, and these figures will be taken in preference to the thermal values.

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[10] Berthelot, M., Ann. chim. phys., **10**, 389 (1877).

A number of interesting oxidation-reduction potentials may be derived from these free energies.

The average oxidation number of dithionic acid is +5, and the following couples give the potential for the change to the +4 and +6 oxidation states.

$$2H_2SO_3 = S_2O_6^{--} + 4H^+ + 2e^-, \qquad E^\circ = -0.20$$

$$2H_2O + S_2O_6^{--} = 2SO_4^{--} + 4H^+ + 2e^-, \qquad E^\circ = -0.20$$

Hence the decomposition reaction,

$$S_2O_6^{--} + H_2O = H_2SO_3 + SO_4^{--}, \qquad \Delta F^\circ = 0.$$

Although the energy of this reaction is favored in alkaline solution, the rate experimentally is greater in acid. If it is presumed correctly that the value chosen for the free energy of $S_2O_6^{--}$ may be too large, the decomposition energy would have a somewhat larger negative value. Yost and Pomeroy[11] have studied the action of oxidizing agents upon dithionate and find it comparatively inert. The reaction rate depends in general upon the rate of the decomposition into sulfurous acid and sulfate, the former being rapidly oxidized.

The conversion of sulfite to dithionate may be carried out by anodic oxidation and is in many ways similar to the oxidation of thiosulfate discussed above. The most efficient pH is about 8, and the overvoltage, or so-called anode polarization, is high. The yield is influenced by the presence of many substances, being high with fluoride and low with Mn^{++}.[12]

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[11] Yost, D. M., and Pomeroy, R., J. Am. Chem. Soc., **49,** 703 (1927).

[12] Cf. Essin, O., Z. Elektrochem., **34,** 78 (1928).

The potential for the oxidation of trithionate and pentathionate are,

$$3H_2O + S_3O_6^{--} = 3H_2SO_3 + 2e^-, \qquad E^\circ = -0.68$$

$$9H_2O + S_5O_6^{--} = 5H_2SO_3 + 8H + 10e^-, \qquad E^\circ = -0.45$$

The reaction mechanisms are doubtless complicated and the overall potentials probably not very significant. Any oxidizing agent capable of oxidizing these thionates will be sufficiently strong to oxidize the sulfurous acid to sulfate.

Since thiosulfate and pentathionate have the same average oxidation number for the sulfur, it is of interest to calculate the free energy of the conversion of thiosulfate to pentathionate.

$$5S_2O_3^{--} + 6H^+ = 2S_5O_6^{--} + 3H_2O, \qquad \Delta F^\circ = -24{,}000 \text{ cal.}$$

The free energy is not large, and considering the obvious complications of the mechanism it is not surprising that the rate of the reaction is slow.

Peroxydisulfate. From the heat of formation of peroxydisulfate, $S_2O_8^{--}$, chosen by Bichowsky and Rossini, and the entropy of formation; assuming the entropy of the ion to be 35 cal. per degree, one calculates the free energy of formation of $H_2S_2O_8$ (or $S_2O_8^{--}$, since it is a strong acid) to be −257,000 cal.

$$2SO_4^{--} = S_2O_8^{--} + 2e^-, \qquad E^\circ = -2.05$$

This value places peroxydisulfate among the most powerful oxidizing agents. The di-acid hydrolyzes to give the mono-acid, H_2SO_5, called "Caro's acid." The data for this acid are insufficient to calculate its free energy. The complete hydrolysis of the di-acid gives hydrogen peroxide,

$$S_2O_8^{--} + 2H_2O = 2H^+ + 2SO_4^{--} + H_2O_2, \qquad \Delta F^\circ = -13{,}300 \text{ cal.}$$

The free energy of the reaction is not large and the reaction is reversed at high concentrations of sulfuric acid and hydrogen peroxide.

Peroxysulfate oxidations are generally slow at ordinary temperature but are catalyzed by silver ion; for example, the oxidation of manganous to permanganate in acid solution. The mechanism of the catalysis has been studied by Yost[13] who found that the rate-determining step was,

$$S_2O_8^{--} + Ag^{+} = 2SO_4^{--} + Ag^{+++},$$

followed by the rapid reduction of the +3 silver ion (cf. p. 181).

The commercial preparation of peroxysulfate is by the anodic oxidation of sulfate, with an electrolyte of either concentrated sulfuric acid (70 per cent) or concentrated ammonium or potassium acid sulfates. Highest efficiency is obtained at low temperatures, 5° to 10° C., high current densities, and smooth platinum electrodes. With sulfuric acid both the mono- and di-acids are formed, and as the concentration of the former builds up, the efficiency decreases, the effect seemingly arising from the depolarizing action, that is, the reaction of the H_2SO_5 with the oxidized surface of the electrode and the consequent lowering of the overvoltage. The presence of fluoride raises the overvoltage and increases the efficiency. At low concentrations of acid, oxygen is evolved, but at high concentrations the activity of the water is lowered to such an extent that the most favorable potential is the oxidation of the sulfate. With the ammonium sulfate process, using as high as 300 g of NH_4HSO_4 per liter, the efficiency is good (70 to 80 per cent) and the process has the added advantage that the ammonium peroxydisulfate separates from the bath because of its lower solubility. This appears to keep down the formation of the monosulfate. The potassium and especially the sodium peroxysulfates are more soluble, and therefore the ammonium sulfate process is generally employed.

The mechanism of the anodic oxidation of sulfate is unknown. It seems likely that it involves the oxidation of the sulfate ion to SO_4^- and the combination of two such ions. The action of fluoride in increasing the efficiency may be through the formation of a fluoride layer on the anode, which thus makes more difficult the evolution of oxygen (cf. oxygen overvoltage).

Sulfur-halogen compounds. There are very little data available for the calculation of the free energy of the many compounds of sulfur with the halogens. Yost and Claussen[14] give −235,000 cal. for the free energy of formation of the hexa-fluoride, SF_6. Potentials for the reduction of the hexa-fluoride in water solution would have but little significance because of its rapid hydrolysis.

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[13] Yost, D. M., J. Am. Chem. Soc., **48**, 152 (1926).

[14] Yost, D. M., and Claussen, W. H., J. Am. Chem. Soc., **55**, 885 (1933).

$$SF_6 + 4H_2O = SO_4^{--} + 8H^+ + 6F^-, \qquad \Delta F^\circ = -108 \text{ kcal.}$$

Lewis and Randall calculate from the work of Trautz[15] that the free energy of formation of sulfuryl chloride (gas) from sulfur dioxide and chlorine is −1900 cal. This, combined with our value for sulfur dioxide, gives −73,600 cal. as the free energy of formation of $SO_2Cl_2(g)$. Its free energy of hydrolysis is,

$$SO_2Cl_2(g) + 2H_2O = SO_4^{--} + 4H^+ + 2Cl^-, \qquad \Delta F^\circ = -51{,}800 \text{ cal.}$$

Bichowsky and Rossini give −14,300 cal. for the heat of formation of $S_2Cl_2(l)$. Estimating the entropy of the compound to be 40, the entropy of formation is −28 cal. per degree, and the free energy of formation is −5900 cal. The potential for the reduction to chloride and sulfur then is,

$$2S + 2Cl^- = S_2Cl_2 + 2e^-, \qquad E^\circ = -1.23.$$

Reduction of sulfur compounds in steps. For convenience, the half-reactions connecting one oxidation state with the higher and lower state have been summarized in Table 15. It is important to keep in mind that these couples are not generally subject to rapid reversibility and hence the potentials, while valuable in many problems, cannot be used in the equilibrium sense. The schematic representation at the foot of Table 15 is useful (see page 74).

Selenium

The standard state of the selenium element is the hexagonal crystalline solid. Two unstable modifications, the red monoclinic and the vitreous, exist. The heat of transition for the former is 200 cal. and for the latter 1100 cal. The heat of sublimation to form the monatomic gas in the $4s^24p^4(^3P_2)$ state is not known. The heat of formation of the Se_2 molecule is given as 29,500 cal., and assuming the same entropy for the reaction as the analogous sulfur reaction, the free energy of formation is 17,800 cal. The gas molecules Se_6 and Se_8 also exist, but the thermal data are too meager for the calculation of their free energies.

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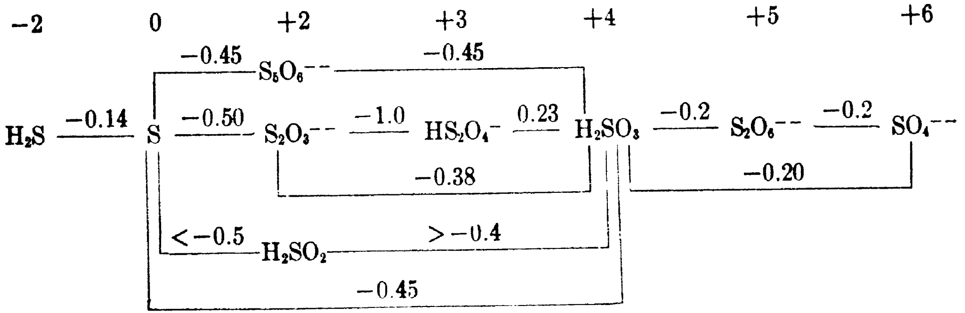
[15] Trautz, M., Z. Elektrochem., **14**, 534 (1908).

TABLE 15

REDUCTION OF SULFUR COMPOUNDS IN STEPS IN ACID SOLUTION

Couple	$E°$
$2SO_4^{--} = S_2O_8^{--} + 2e^-$	−2.05
$2H_2O + S_2O_6^{--} = 2SO_4^{--} + 4H^+ + 2e^-$	−0.20
$2H_2SO_3 = S_2O_6^{--} + 4H^+ + 2e^-$	−0.20
$2H_2O + HS_2O_4^- = 2H_2SO_3 + H^+ + 2e^-$	+0.23
$H_2O + S_2O_3^{--} = HS_2O_4^- + H^+ + 2e^-$	−1.03
$3H_2O + 2S = S_2O_3^{--} + 6H^+ + 4e^-$	−0.50
$H_2S = S + 2H^+ + 2e^-$	−0.141

POTENTIAL DIAGRAM FOR THE OXIDATION STATES OF SULFUR



Oxidation states. The oxidation state of selenium is −2 in the selenides, +4 in selenites, and +6 in selenates. Oxygen compounds corresponding to the +2, +3, +5 states and the poly-acids of sulfur are not known. Polyselenides as $NaSe_2$ and $NaSe_3$ exist but are less stable than the polysulfides. Compounds with the halogens are, in general, similar to those of sulfur with the halogens.

The selenide-selenium couple. Bichowsky and Rossini give 18,500 cal. as the heat of formation of $H_2Se(g)$. From analogy to the entropy of formation of H_2S, the value 10.6 will be used for the entropy of formation of $H_2Se(g)$. Hence, the free energy of formation is 15,300 cal. McAmis and Felsing[16] found 1421 cal. for the free energy of solution. Bruner[17] found 1.7×10^{-4} as the first dissociation constant for aqueous hydrogen selenide. The second constant is not known, but a value of 10^{-10} is probably not far off. We then find the following free energies: $H_2Se(aq)$, 16,720 cal.; HSe^-, 22,120 cal.; and Se^{--}, 35,760 cal. If one calculates the free energy of Se^{--} from the accepted heat of formation and any reasonable assumption for its entropy, the value obtained is at least 10,000 cal. greater; hence, it would appear that the heats of neutralization of H_2Se are in error by this amount. These values lead to the following potentials:

$$H_2Se(aq) = Se + 2H^+ + 2e^-, \qquad E^\circ = 0.36$$

$$Se^{--} = Se + 2e^-, \qquad E^\circ_B = 0.78.$$

The selenides are thus unstable with respect to the oxidation by hydrogen ion but the reaction appears to be slow.

The selenium-selenite couple. Schott, Swift, and Yost[18] have determined the potential of the selenium-selenite couple in water solutions by direct equilibrium methods. They found for the free energies: $H_2SeO_3(aq)$, −101,361 cal.; $HSeO_3^-$, −97,850 cal.; and SeO_3^{--}, −87,890 cal. These values are in close agreement with the thermal data. The potentials are:

$$Se + 3H_2O = H_2SeO_3 + 4H^+ + 4e^-, \qquad E^\circ = -0.740$$

$$6OH^- + Se = SeO_3^{--} + 3H_2O + 4e^-, \qquad E^\circ_B = 0.35.$$

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[16] McAmis, A. J., and Felsing, W. A., J. Am. Chem. Soc., **47**, 2633 (1925).

[17] Bruner, L., Z. Elektrochem., **19**, 861 (1913).

[18] Schott, H. F., Swift, E. H., and Yost, D. M., J. Am. Chem. Soc., **50**, 721 (1928).

From the fact that they were able to get equilibrium with iodide and iodine, the couple is reversible and fairly rapid.

Selenite-selenate couple. Sherrill and Izard[19] measured the equilibrium between the selenite-selenate couple and the chloride-chlorine and bromide-bromine couples. From their work, one calculates 107,840 cal. as the free energy of $HSeO_4^-$. Using the dissociation constant 10^{-2}, the free energy of SeO_4^{--} is 105,120 cal. This value will be used for both the ion and the acid, but in actual solution the correction for the $HSeO_4^-$ should be made. The heat of formation of SeO_4^{--} is given as $-146,400$ cal. Estimating 135 as the entropy of formation in comparison to 133 for SO_4^{--}, the calculated free energy is 105,900 cal., in good agreement with the value from the equilibrium data. The potentials are:

$$H_2O + H_2SeO_3 = SeO_4^{--} + 4H^+ + 2e^-, \qquad E^\circ = -1.15$$

$$2OH^- + SeO_3^{--} = SeO_4^{--} + H_2O + 2e^-, \qquad E^\circ_B = -0.03.$$

Since equilibrium was established with the chlorine couple in four to seven days and with the bromine couple in fifty to seventy days, selenic acid is not a very rapid oxidizing agent. For some unknown reason the reduction with halide ions is faster than with more powerful reducing agents. For example, there is no appreciable reduction with H_2S, SO_2, or Fe^{++}.

Selenium halogen compounds. Yost and Claussen[20] reported $-246,000$ cal. as the heat of formation of selenium hexafluoride gas. Using the same ΔS° as for the sulfur hexafluoride, -90 cal. per degree, the free energy is $-219,000$ cal. and the free energy of its hydrolysis would be

$$SeF_6(g) + 4H_2O = SeO_4^{--} + 8H^+ + 6F^-, \qquad \Delta F^\circ = -53 \text{ kcal.}$$

Bichowsky and Rossini give -22.13 kcal. as the heat of formation of $Se_2Cl_2(l)$. Using the same entropy of formation as for the corresponding sulfur compound, -28 cal. per degree, the free energy of formation is $-13,730$ cal. The potential for reduction to chloride and selenium then is,

$$2Se + 2Cl^- = Se_2Cl_2 + 2e^-, \qquad E^\circ = -1.06.$$

Similar calculations may be made for $SeCl_2$ and $SeCl_4$.

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[19] Sherrill, M. S., and Izard, E. F., J. Am. Chem. Soc., **50**, 1665 (1928).

[20] Yost, D. M., and Claussen, W. H., J. Am. Chem. Soc., **55**, 885 (1933).

Tellurium

The standard state of the tellurium element is the crystalline solid. An unstable amorphous form is common. The heat of transition of the amorphous or precipitated tellurium is given as 2.7 kcal. From the Bichowsky and Rossini values for the heat of formation of the monatomic atom and the diatomic molecule, together with the entropy data, one calculates for the free energy of Te(g), 46.0 kcal. and $Te_2(g)$, 12.3 kcal.

Oxidation states. Like selenium, the −2, +4, and +6 oxidation states of tellurium are the only ones of importance. The +2 oxide, TeO, exists, and in cold hydrochloric acid it appears to form the salt $TeCl_2$, but when the solution is warmed it decomposes into the free element and a +4 complex chloride.

The telluride-tellurium couple. The heat of formation of hydrogen telluride gas, H_2Te, is given as 34,200 cal. The entropy is not known experimentally, but the estimated entropy of formation of 10.6 cal. per degree is doubtless more accurate than the value for the heat. From these values the free energy of formation of $H_2Te(g)$ is 31,000 cal. The free energy of solution appears to be about 1000 cal. Hence the free energy of $H_2Te(aq)$ is 32,000 cal., and

$$H_2Te(aq) = Te + 2H^+ + 2e^-, \qquad E^\circ = 0.69.$$

De Hlasko[21] gave 0.0023 for the first dissociation constant of the acid. For the second constant, Kasarnowsky[22] guessed 2.5×10^{-4}, but 10^{-5} would seem to be a maximum. From these "data" the probable value for the free energy of HTe^- appears to be 35,500 cal. and of Te^{--}, 42,300 cal.

$$Te^{--} = Te + 2e^-, \qquad E_B^\circ = 0.92$$

Kasarnowsky reports from direct cell measurements,

$$Te_2^{--} = 2Te + 2e^-, \qquad E^\circ = 0.84$$

from which the free energy of Te_2^{--} is 38,750 cal. From the two half-reactions one calculates

$$Te^{--} + Te = Te_2^{--}, \qquad \Delta F^\circ = -3550 \text{ cal.}$$

The value for this free energy appears reasonable. As the high positive potentials indicate, −2 tellurium is a powerful reducing agent, and much of the difficulty in obtaining accurate data on these compounds arises from the inability of the experimenters to prevent some oxidation.

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[21] De Hlasko, M., J. chim. phys., **20,** 167 (1923).

[22] Kasarnowsky, J., Z. anorg. allgem. Chem., **128,** 32 (1923).

The tellurium-tellurous acid couple. Schuhmann[23] has determined by direct measurement the following couples:

$$2H_2O + Te = TeO_2(s) + 4H^+ + 4e^-, \quad E° = -0.529$$

$$2H_2O + Te = TeOOH^+ + 3H^+ + 4e^-, \quad E° = -0.559.$$

The corresponding free energy values are $TeO_2(s)$, −64,530 cal. and $TeOOH^+$, −62,480 cal. This author also gave TeO_2 as the stable solid in equilibrium with water and reported,

$$TeO_2 + H^+ = TeOOH^+, \qquad K = 8.9 \times 10^{-3}$$

$$TeO_2 + H_2O = TeOOH^+ + OH^-, \qquad K = 8.9 \times 10^{-17}$$

Kasarnowsky[24] gave

$$TeO_2(s) + H_2O = H_2TeO_3(s), \qquad \Delta F = 5550 \text{ cal.}$$

From these values one calculates for the free energy of the H_2TeO_3, −115,670 cal. and for the basic dissociation of $TeO(OH)_2$,

$$TeO(OH)_2(s) = TeOOH^+ + OH^-, \qquad K = 1 \times 10^{-11}.$$

Blanc[25] reported $K_1 = 2 \times 10^{-3}$ and $K_2 = 1 \times 10^{-8}$ for the two acid constants, but there are no accurate data on the solubility of the acid in water. The free energy of the ion TeO_3^{--} could be calculated directly from the heat of formation, −141,000 cal., if its entropy were known. Estimating −5 as this value, the calculated free energy is −104,500 cal.

$$6OH^- + Te = TeO_3^{--} + 3H_2O + 4e^-, \quad E_B^\circ = 0.02.$$

The tellurous acid-telluric acid couple. From the thermal data tabulated by Bichowsky and Rossini,

$$4H_2O(l) + TeO_2(s) = H_6TeO_6(s) + H_2, \qquad \Delta H° = 45,600 \text{ cal.}$$

The entropies of TeO_2 and H_6TeO_6 are not known, but from similar compounds the values 16 and 47 are estimated. ΔS° for the reaction is -5 cal. per degree and $\Delta F^\circ = 47{,}100$ cal.

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[23] Schuhmann, R., J. Am. Chem. Soc., **47**, 356 (1925).

[24] Ksarnowsky, J., Z. physik. Chem., **109**, 287 (1924).

[25] Blanc, E., J. chim. phys., **18**, 28 (1920).

$$4H_2O + TeO_2 = H_6TeO_6(s) + 2H^+ + 2e^-, \qquad E^\circ = -1.02$$

The free energy of solution of the orthotelluric acid is not known but it does not appear to be large, and this value for the solid can be used for any approximate calculations. The calculated potential is consistent with the fact that oxidizing agents of about the strength of chlorine are required to oxidize tellurous acid to telluric. Thermal data on the meta-acid H_2TeO_4 and the ion TeO_4^{--} give results which are in disagreement with chemical properties, hence it is impossible to give a potential for the tellurite-tellurate couple in alkaline solution. However, hypoiodite is capable of oxidizing tellurite, hence

$$2OH^- + TeO_3^{--} = TeO_4^{--} + H_2O + 2e^-, \qquad E_B^\circ > -0.4.$$

Like selenic acid, telluric acid is reduced much more readily by halide ions than by more powerful reducing agents, such as stannous and sulfur dioxide.

Halogen compounds of tellurium. Using the heats of reactions and entropy values similar to those employed for the analogous sulfur compounds, free energies may be calculated for TeF_6, $TeCl_4$, and $TeBr_4$. The complex ions $TeCl_6^{--}$ and $TeBr_6^{--}$ exist in water solutions at moderate concentration of halide ions; and salts, such as $(NH_4)_2TeCl_6$, may be crystallized. Reichinstein[26] has measured the potential of tellurium against solutions of $TeCl_4$ in 2.5 M HCl. Although the complex ion formula is uncertain, we shall write from his results

$$6Cl^- + Te = TeCl_6^{--} + 4e^-, \qquad E^\circ = -0.55.$$

This would make the free energy of $TeCl_6^{--}$ $-137{,}400$ cal. If one calculates the free energy of $TeCl_4(s)$ from thermal data, assuming the entropy of the $TeCl_4$ to be 52, the free energy of the $TeCl_4$ is $-57{,}400$ cal., and hence

$$TeCl_4(s) + 2Cl^- = TeCl_6^{--}, \qquad \Delta F = -17{,}300 \text{ cal.}$$

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[26] Reichinstein, D., Z. physik. Chem., **97**, 257 (1921).

This equation is subject to a reinterpretation of the formula of the complex ion in Reichinstein's investigation.

Polonium

The standard state of the polonium element is the metallic solid. Nothing is known with regard to its thermal properties, as it has never been isolated in sufficient quantity to study.

Oxidation states. Our knowledge of the chemistry of polonium is based upon its radioactive properties, in the sense that its behavior toward various reagents can be studied by observing whether the activity goes with the precipitate or remains in solution. It forms a very unstable hydrogen compound, H_2Po, -2 state, and appears to exist in water solution as $+2$ polonium, Po^{++}. The oxidation state of $+4$ occurs in PoO_2.

TABLE 16

POTENTIAL VALUES RELATING THE IMPORTANT OXIDATION STATES OF GROUP VI IN ACID SOLUTION

-2		0		$+4$		$+6$
H_2O	-1.23	O_2				
H_2S	-0.14	S	-0.45	$H_2SO_3(aq)$	-0.20	SO_4^{--}
H_2Se	0.35	Se	-0.74	$H_2SeO_3(aq)$	-1.15	SeO_4^{--}
H_2Te	0.69	Te	-0.53	$TeO_2(s)$	-1.02	$H_6TeO_6(s)$
H_2Po	>1.0	Po	-0.74	$PoO_2(s)$	$-1.5(?)$	$PoO_3(s)(?)$

Polonium couples. From its chemical behavior, one estimates,

$$H_2Po(g) = Po + 2H^+ + 2e^-, \qquad E^\circ > 1.0.$$

Paneth and Hevesy[27] and Haissinsky[28] have studied the potentials for the cathodic reduction of polonium to the metal and the anodic oxidation to the dioxide. From their work the probable values seem to be,

$$Po = Po^{++} + 2e^-, \qquad E^\circ = -0.65$$

$$2H_2O + Po^{++} = PoO_2 + 4H^+ + 2e^-, \qquad E^\circ = -0.8$$

$$6OH^- + Po = PoO_3^{--} + 3H_2O + 4e^-, \qquad E_B^\circ = 0.5$$

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[27] Paneth, F., and Hevesy, G. v., Monatsh., **34**, 1593 (1913).

[28] Haissinsky, M., J. chim. phys., **29**, 453 (1932).

The corresponding free energies are: Po^{++}, 30,000 cal.; PoO_2, −106,000 cal.; PoO_3^{--}, −102,000 cal.; and $H_2Po(g)$, > 46,000 cal.

Summary of Group VI potentials. In order to show the trends exhibited by the oxidation-reduction potentials in the group, the values relating the −2, 0, +4, and +6 oxidation states have been summarized in Table 16.

The most striking characteristic of these potentials is the decrease in the power of the free elements as oxidizing agents. The acids of the +4 and +6 states increase in oxidizing power with increasing atomic weight with the exception that the potentials of the selenium acids are unduly high.

CHAPTER VII

Nitrogen, Phosphorus, Arsenic, Antimony, and Bismuth

The elements of Group V of the periodic system vary in properties from highly electronegative nonmetallic nitrogen to distinctly metallic bismuth. The stability of the -3 oxidation state decreases sharply as the atomic weight increases. In the $+3$ and $+5$ states of the oxygen acids, the elements are good oxidizing agents except in the case of phosphorus. The most powerful oxidizing agent of the group is the $+5$ bismic acid. The normal electronic state of the atoms of the group is $s^2p^3(^4S_{3/2})$.

Nitrogen

The standard state of the element is the gas N_2. Herzberg and Sponer[1] report 7.34 volt-electrons as the dissociation energy; and this, together with the entropy of dissociation (13.73 cal. per degree), gives 81,000 cal. as the free energy of atomic nitrogen.

The oxidation states. Nitrogen forms compounds having all the oxidation states from -3 to $+5$. The most important compounds in the various states are: -3, ammonia, NH_3; -2, hydrazine, N_2H_4; -1, hydroxylamine, NH_2OH; $+1$, nitrous oxide, N_2O and hyponitrous acid, $H_2N_2O_2$; $+2$, nitric oxide, NO; $+3$, nitrous acid, HNO_2; $+4$, nitrogen dioxide, NO_2 and nitrogen tetroxide, N_2O_4; and $+5$, nitric acid, HNO_3. In general, the compounds of the even numbers contain an even number of nitrogen atoms, but nitric oxide is an odd molecule and possesses but slight tendency to form a double molecule. Very few compounds are known in which the average oxidation number of the nitrogen is fractional. Hydrazoic acid, HN_3, is an example of such a compound.

Free energies from thermal data. Lewis and Randall summarized the data on several important equilibria involving nitrogen compounds and gave values for the free energies of a number of these compounds. The entropies of many nitrogen compounds are now known with accuracy, so that a more reliable set of free energies may be obtained employing the Third Law of Thermodynamics. For convenience in later calculation, data on the free energies of formation are summarized in Table 17.

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[1] Herzberg, G., and Sponer, H., Z. physik. Chem., **B 26**, 1 (1934).

The thermal data for the nitrogen oxides are from Giauque and Kemp.[2] Other heats of formation are taken from Bichowsky and Rossini, with the exception that 25,600 has been used for NO_2^- instead of their 25,300. There is still considerable uncertainty in some of the heats, especially for nitric oxide, but in general the third law values are to be preferred to those obtained from equilibrium data. The entropy of hydroxylamine, NH_2OH(aq), has been estimated as 40 in comparison with 43 for NH_4OH; N_2H_4(aq) as 33 in comparison with 26 for NH_3(aq); $H_2N_2O_2$ as 52 in comparison with 55 for H_2SO_3; and HN_3 as 48 against 50 for HNO_2. There are no equilibrium values for these compounds, and errors in the heats of formation are probably greater than the errors in the estimated entropies.

TABLE 17
FREE ENERGIES OF FORMATION OF NITROGEN COMPOUNDS

Compound	$\Delta H°$	$\Delta S°$	$\Delta F°$ (Third Law)	$\Delta F°$ (L and R)
NO(g)	21,530	2.9	20,660	20,850
N_2O(g)	19,650	−17.7	24,930	.
NO_2(g)	7,964	−14.5	12,274	11,920
N_2O_4(g)	2,239	−71.1	23,440	22,640
NO_3^-	−49,190	−77.1	−26,250	−26,500
NO_2^-	−25,600	−57.5	−8,450	−8,500
NH_3(g)	−11,000	−23.7	−3,940	−3,910
N_2H_4(aq)	4,500	(−85.0)	29,800	...
NH_2OH(aq)	−21,700	(−54.0)	−5,600	...
$H_2N_2O_2$(aq)	−8,400	(−74.0)	13,600	. .
HN_3(aq)	54,600	(−36.0)	65,300	. .
NOCl(g)	12,800	−13.3	16,750	16,010

Equilibria involving HNO_3, HNO_2, N_2O_4, NO_2, and NO. From Table 17, the free energy of nitrite ion is −8450 cal. Schümann[3] reported 0.00045 for the ionization constant of nitrous acid. This makes the free energy of ionization 4570 cal. and the free energy of formation of nitrous acid −13,020 cal. From Table 17 the free energy of nitrate ion is −26,250 cal. Nitric acid will be treated as completely dissociated, so the same value is used for the acid. Before discussing nitric and nitrous acid potentials, a number of equilibria should be considered.

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[2] Giauque, W. F., and Kemp, J. D., J. Chem. Phys., **6**, 40 (1938).

[3] Schümann, M., Ber., **33**, 527 (1900).

From Table 17,

$$2NO_2 = N_2O_4, \qquad \Delta F^\circ = -1110 \text{ cal.},$$

and the equilibrium constant for the reaction is 6.5. Hence at 25° C. the equilibrium mixture is largely N_2O_4 and equations will generally be written with tetroxide instead of the dioxide.

In alkaline solution, nitrogen tetroxide is unstable with respect to the decomposition into nitrite and nitrate,

$$N_2O_4 + 2OH^- = NO_2^- + NO_3^- + H_2O, \quad \Delta F^\circ = -39{,}660 \text{ cal.}$$

In cold water, low concentrations of N_2O_4 react to form a blue solution of nitric and nitrous acids. The free energy at 25° C. is

$$N_2O_4 + H_2O = HNO_2 + H^+ + NO_3^-, \qquad \Delta F^\circ = -6020 \text{ cal.}$$

However in concentrated nitric acid the reaction is reversed and nitrous acid is oxidized to the tetroxide.

From the free energies of Table 17 we may also calculate,

$$2HNO_2 = NO + NO_2 + H_2O, \qquad \Delta F^\circ = 2280 \text{ cal.}$$

This small positive free energy shows that there is a very appreciable pressure of NO and NO_2 in equilibrium with a nitrous acid solution, but a still more important reaction is the decomposition of nitrous acid into nitric acid and nitric oxide,

$$3HNO_2 = H^+ + NO_3^- + 2NO + H_2O, \ \Delta F^\circ = -2260 \text{ cal.}$$

The direct experimental value for the equilibrium constant leads to a free energy of −2040 cal. as calculated by Lewis and Randall. The rate of the reaction is not rapid in cold dilute solutions of nitrous acid, but it becomes so upon heating. Hence, in warm concentrated solutions of the tetroxide the principal equilibrium is the following:

$$3NO_2 + H_2O = 2NO_3^- + 2H^+ + NO, \qquad \Delta F^\circ = -10{,}800 \text{ cal.}$$

The free energy is not large however, and nitric oxide passed into concentrated nitric acid would obviously form an appreciable amount of NO_2 or N_2O_4.

The reduction of nitric acid. From the above equilibria it follows that the reduction products, obtained upon the addition of a reducing agent to an excess of nitric acid, will depend very largely upon the concentration of the nitric acid. In many cases the first step is doubtless the reduction to nitrous acid,

$$H_2O + HNO_2 = NO_3^- + 3H^+ + 2e^-, \qquad E^\circ = -0.94.$$

But at low acid concentration, because of the decomposition of the nitrous acid, the net reaction is,

$$2H_2O + NO = NO_3^- + 4H^+ + 3e^-, \qquad E^\circ = -0.96$$

and at high acid concentrations,

$$2H_2O + N_2O_4 = 2NO_3^- + 4H^+ + 2e^-, \qquad E^\circ = -0.81.$$

The potential of this last couple changes rapidly with the concentration of hydrogen ion. Concentrated nitric acid is a rapid and powerful oxidizing agent, but in low hydrogen ion it is not only weak but also very slow in its reaction rate.

As an example of the effect of concentration upon the reduction products, one may cite the reduction of nitric acid by arsenious acid: with HNO_3 of density 1.45 the product is 1 part NO and 5 parts N_2O_4; with acid of density 1.35, the composition corresponds to N_2O_3 ($NO + NO_2$) and an acid density of 1.20 gives almost pure NO.

In view of these potentials, a powerful oxidizing agent is required to oxidize nitrous acid to nitric acid, and the reaction is quantitative with permanganate. Nitric oxide is, of course, readily oxidized to N_2O_4 by molecular oxygen, but it is remarkably inert to oxidation by many powerful agents, although PbO_2, MnO_2, and $KMnO_4$ will oxidize it slowly to nitric acid.

The nitrogen-tetroxide couples in acid solution are,

$$2HNO_2 = N_2O_4 + 2H^+ + 2e^-, \qquad E^\circ = -1.07$$

$$2H_2O + 2NO = N_2O_4 + 4H^+ + 4e^-, \qquad E^\circ = -1.03.$$

These values place the tetroxide about equal to bromine as an oxidizing agent in molal acid solution. Its action is much more rapid in general than nitric acid.

The nitrite-nitrate couple. Because of the decomposition of nitrogen tetroxide in alkali and of the greater stability of nitrite ion, the net half-reaction for the reduction of nitrate ion in hydroxide solution is,

$$2OH^- + NO_2^- = NO_3^- + H_2O + 2e^-, \qquad E^\circ_B = -0.01.$$

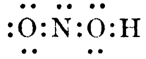
The reduction of nitrate is slow with many reducing agents, but it goes with sodium amalgam and with ferrous hydroxide, and it may also be carried out electrolytically with copper or silver cathodes. Because of the more rapid reduction of nitrite, it is difficult to stop the reaction at the nitrite state even when no excess of reducing agent is used. The presence of cupric ions appears to favor the electrolytic reduction to nitrite in neutral solution, but lead ion catalyzes the reduction to lower oxidation states.

Nitrite may be oxidized to nitrate by comparatively weak oxidizing agents and also by anodic oxidation. The rate of the latter reaction is favored by low hydroxide concentration, contrary to the prediction from the overall reaction potentials. However the mechanism of the reaction is unknown and the accompanying oxidation of the water to oxygen is also favored by high hydroxide concentration.

The reduction of nitrous acid. Ferrous ion, a weak reducing agent, and titanous ion, a powerful reducing agent, both reduce nitrous acid to nitric oxide; while stannous ion, which is intermediate in potential, reduces nitrous acid to hydroxylamine when the solution is cold, and to nitrous oxide when the solution is hot. The first two are one-electron reducing agents, and the reduction to nitric oxide involves but one electron. Because of the remarkable inertness of nitric oxide, the reaction stops at this point. The potential of the nitric oxide-nitrous acid couple is,

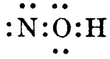
$$H_2O + NO = HNO_2 + H^+ + e^-, \qquad E^\circ = -0.99.$$

It is generally assumed that two-electron reducing agents such as stannous ion first form with nitrous acid some intermediate compound of +1 oxidation number. Both nitrous oxide, N_2O, and hyponitrous acid, $H_2N_2O_2$, correspond to this state, but the intermediate is thought to be nitroxyl, NOH, or possibly dihydroxylammonia, $NH(OH)_2$. From the electron structures the latter seems somewhat more reasonable, as it does not involve breaking an oxygen-nitrogen bond.



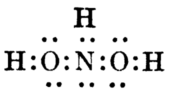
$$:\ddot{\underset{..}{O}}:\ddot{N}:\ddot{\underset{..}{O}}:H$$

(nitrous acid)



$$:\ddot{N}:\ddot{\underset{..}{O}}:H$$

(nitroxyl)



$$H:\ddot{\underset{..}{O}}:\overset{H}{\underset{..}{\overset{..}{N}}}:\ddot{\underset{..}{O}}:H$$

(dihydroxylammonia)

Harteck[4] has prepared a form of HNO by the reaction of atomic hydrogen with nitric oxide, and atomic oxygen with ammonia at liquid air temperature. He has also claimed the preparation of NaNO by the reaction of sodium and nitric oxide in liquid ammonia.

The free energies of NOH and $NH(OH)_2$ are not known. The calculated free energy of hyponitrous acid (see Table 17) depends upon the determination of Berthelot[5] of the heat evolved in the oxidation of hyponitrous acid to nitric acid by bromine. The small positive value of the free energy seems fairly reasonable, but it leads to a very large free energy for the decomposition of hyponitrous acid to nitrous oxide.

$$H_2N_2O_2 = N_2O + H_2O, \qquad \Delta F^\circ = -45{,}360 \text{ cal.}$$

The reaction is known to be irreversible, as the high free energy indicates, but it is quite possible that our value for the free energy of $H_2N_2O_2$ is somewhat too positive, and the decomposition energy is smaller than -45 kcal. It would seem that the potential for the reduction of nitrous acid to nitroxyl would be more nearly equal to that of the hyponitrous acid–nitrous acid couple than to the nitrous oxide–nitrous acid couple since nitroxyl must also be very unstable with respect to its decomposition to form nitrous oxide.

$$2H_2O + H_2N_2O_2 = 2HNO_2 + 4H^+ + 4e^-, \qquad E^\circ = -0.80$$

$$3H_2O + N_2O = 2HNO_2 + 4H^+ + 4e^-, \qquad E^\circ = -1.29$$

Similarly the reduction of hyponitrous acid to hydroxylamine should be a fair approximation for the corresponding reduction of NOH.

$$2NH_3OH^+ = H_2N_2O_2 + 6H^+ + 4e^-, \qquad E^\circ = -0.44$$

This small negative value should constitute a barrier to the reduction of nitrous acid to hydroxylamine by weak reducing agents. The ionization constants of $H_2N_2O_2$ are said to be similar to those of carbonic acid.

The free energy of hydroxylamine is given in Table 17, and the value for the acid ion is obtained from the basic ionization constant given by Winkelbleck.[6]

$$NH_2OH(aq) + H_2O = NH_3OH^+ + OH^-, \qquad K = 6.6 \times 10^{-9}$$

This leads to $-13{,}540$ cal. as the free energy of NH_3OH^+.

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[4] Harteck, P., Ber., **66**, 423, 768 (1933).

[5] Berthelot, M., Ann. chim. phys., **18**, 571 (1889).

[6] Winkelbleck, K., Z. physik. Chem., **36**, 574 (1901).

Bray, Simpson, and MacKenzie[7] have studied the oxidation of hydroxylamine by ferric ion which is powerful enough to oxidize it to NOH but does not oxidize NOH to HNO_2. They found that at high acid concentrations the product was quantitatively N_2O, the mechanism probably being the formation of NOH and its decomposition into nitrous oxide,

$$2NOH = N_2O + H_2O.$$

At low hydrogen ion, nitrogen was formed, presumably through the reaction,

$$NH_3OH^+ + NOH = N_2 + 2H_2O + H^+.$$

The faster rate of decomposition of nitroxyl in acid may arise from its slightly basic character and the formation of N^+ which then reacts with NOH to link the nitrogens together. The ordinary splitting out of water between two nitroxyl molecules would produce N-O-N and not N-NO which is the actual atomic arrangement in nitrous oxide.

More powerful oxidizing agents than ferric ion will, of course, oxidize hydroxylamine to nitrous acid. Under these conditions nitrous oxide may be formed by the reaction,

$$HNO_2 + NH_3OH^+ = N_2O + 2H_2O + H^+, \quad \Delta F^\circ = -61.9 \text{ kcal.}$$

Under suitable conditions the product is hyponitrous acid,

$$HNO_2 + NH_3OH^+ = H_2N_2O_2 + H_2O + H^+, \quad \Delta F^\circ = -16.5 \text{ kcal.}$$

A possible mechanism for the formation of nitric oxide by the reduction of nitrous acid is through nitroxyl and its reaction with the excess nitrous acid,

$$NOH + HNO_2 = 2NO + H_2O.$$

However it is doubtful whether this is the case with the one-electron reducing agent such as titanous ion, but it may be the explanation of the action of stannous ion. With an excess of this reagent in low acid, nitrous oxide is formed; but with excess nitrous acid, nitric oxide results (cf. Raschig[8]).

There is some evidence of the existence of nitrohydroxylamic acid, $H_2N_2O_3$, in which the nitrogen is also in the +2 oxidation state. The acid is considered to be unstable with respect to the decomposition into nitric oxide and water. The role which it plays, if any, in the oxidation of nitroxyl or the reduction of nitrous acid is unknown.

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[7] Bray, W. C., Simpson, M. E., and MacKenzie, A. A., J. Am. Chem. Soc., **41**, 1363 (1919).

[8] Raschig, F., Z. anorg. allgem. Chem., **155**, 225 (1926).

The hydroxylamine-ammonium couple. Combining the free energy value of ammonia gas (Table 17) with the values chosen by Lewis and Randall for the free energy of solution and the free energy of ionization of ammonium hydroxide ($K = 1.81 \times 10^{-5}$), one obtains the following free energies: $NH_3(aq)$, -6330 cal.; NH_4OH, $-62{,}990$ cal.; and NH_4^+, $-18{,}960$ cal. The potential for the hydroxylamine-ammonium ion couple then is,

$$H_2O + NH_4^+ = NH_3OH^+ + 2H^+ + 2e^-, \qquad E^\circ = -1.35.$$

This value would indicate that hydroxylamine is a powerful oxidizing agent, but actually its rate of reduction is slow with many powerful reducing agents. For example there appears to be no reduction with stannous ion in acid solution. The reaction does go in acid, however, with zinc, ferrous, and titanous. On the other hand, very powerful oxidizing agents are required to oxidize ammonium ion as the potential requires, and in general any oxidizing agent which will oxidize ammonium ion to hydroxylamine will take it on up to nitric acid.

Hydroxylamine is unstable with respect to the decomposition into ammonium ion and nitrous oxide,

$$4NH_3OH^+ = N_2O + 2NH_4^+ + 3H_2O + 2H^+, \Delta F^\circ = -118{,}900 \text{ cal.},$$

and the reaction is favored by alkali as the equation indicates. The mechanism is doubtless through nitroxyl so that some nitrogen may also be formed simultaneously by the reaction of the NOH with NH_3OH^+ as discussed above.

Bancroft[9] has presented evidence that nitrous acid may be reduced to ammonium without going through the hydroxylamine stage. As a hypothetical mechanism the formation of NH or N_2H_2 might be assumed. But this substance would certainly have a more positive free energy than hydroxylamine so that the reduction from the +1 to the −1 state would be difficult. It is, however, a possible process with powerful reducing agents.

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[9] Bancroft, W. D., J. Phys. Chem., **28**, 475 (1924).

The reduction of nitrous acid with sulfite. The one reducing agent for which the mechanism of the reduction of nitrous acid is best understood is sulfurous acid. The intermediate compounds are shown in the following scheme.

STEPS IN THE REDUCTION OF NITROUS ACID WITH SULFITE

$$\begin{tikzcd}
HNO_2 \arrow[d, "\text{with } HSO_3^-"'] & \\
\underset{\text{(nitrosulfonic acid)}}{HSO_3\cdot NO} \arrow[r, dashed, "\text{with } H^+"] \arrow[d, "\text{with } HSO_3^-"'] & \underset{\text{(hyponitrous acid)}}{HNO(H_2N_2O_2)} \\
\underset{\substack{\text{(hydroxylamine}\\\text{disulfonic acid)}}}{(HSO_3)_2\cdot NOH} \arrow[r, dashed, "\text{with } H^+"] \arrow[d, "\text{with } HSO_3^-"'] & \underset{\text{(hydroxylamine)}}{NH_3OH^+} \\
\underset{\text{(nitrilosulfonic acid)}}{(HSO_3)_3\cdot N} \arrow[r, dashed, "\text{with } H^+"] & \underset{\text{(ammonium)}}{NH_4^+}
\end{tikzcd}$$

The reactions with HSO_3^- are reversed in high hydroxide concentrations. With H^+, hydrolysis occurs with the formation of sulfuric acid and the products indicated by the arrows. These reactions may be looked upon as the successive replacement of the OH radical in orthonitrous acid $N(OH)_3$ by HSO_3 radicals and these in turn by H upon hydrolysis. The result is a series of two-electron reductions. Similarly the reduction of nitric acid, $HONO_2$, with sulfurous acid first forms nitrosyl sulfuric acid, HSO_3NO_2, which hydrolyses to nitrous and sulfuric acids. At high hydrogen ion, nitrous acid is reduced by sulfurous acid to nitrous oxide.

The oxidation and reduction of hydrazine. The basic dissociations of hydrazine are given by Schwarzenbach[10] as $K_1 = 8.5 \times 10^{-7}$ and $K_2 = 8.9 \times 10^{-16}$. Combining the corresponding free energies with that of hydrazine from Table 17, we obtain the resulting free energies: $N_2H_5^+$, 18,950 cal., and $N_2H_6^{++}$, 20,450 cal. From these values, the potentials of the following half-reactions may be calculated:

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[10] Schwarzenbach, G., Helv. Chem. Acta, **19**, 178 (1936).

$$2NH_4^+ = N_2H_5^+ + 3H^+ + 2e^-, \qquad E^\circ = -1.24$$

$$2OH^- + 2NH_4OH = N_2H_4 + 4H_2O + 2e^-, \qquad E_B^\circ = -0.1$$

$$2H_2O + N_2H_5^+ = 2NH_3OH^+ + H^+ + 2e^-, \qquad E^\circ = -1.46$$

$$2OH^- + N_2H_4 = 2NH_2OH + 2e^-, \qquad E_B^\circ = -0.74$$

$$N_2H_5^+ = N_2 + 5H^+ + 4e^-, \qquad E^\circ = 0.17$$

$$4OH^- + N_2H_4 = N_2 + 4H_2O + 4e^-, \qquad E_B^\circ = 1.15$$

It is obvious that hydrazine in acid solution should be a powerful oxidizing agent. The reaction rate is very slow, but it may be titrated quantitatively with strong reducing agents. However, powerful oxidizing agents are required to oxidize ammonia to hydrazine, chlorine being generally employed. In this oxidation the ammonia must be in excess to prevent the further oxidation of the hydrazine which goes very readily to nitrogen as the half-reaction potential indicates. The potential for the oxidation of hydrazine to hydroxylamine is very high, and there is no evidence that the reaction ever occurs.

Bray and Cuy[11] studied the oxidation of hydrazine and found that while the oxidation to nitrogen is quantitative with some reagents (as, for example, with iodine) one-electron oxidizing agents tend, as a limit, to form two molecules of NH_4^+ and one of N_2. As a mechanism Bray and Cuy assumed that N_2H_3 is the first product and that it decomposes according to the equation,

$$2H^+ + 2N_2H_3 = N_2 + 2NH_4^+.$$

The oxidation takes place with ferric ion, so the N_2H_3 must be a weaker oxidizing agent than this substance,

$$N_2H_5^+ = N_2H_3 + 2H^+ + e^-, \qquad E^\circ > -0.6$$

As the potential values predict, hydrazine is capable of oxidizing and reducing itself to form nitrogen and ammonia,

$$3N_2H_4 = N_2 + 4NH_3, \qquad \Delta F^\circ = -114{,}700 \text{ cal.}$$

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[11] Bray, W. C., and Cuy, E. J., J. Am. Chem. Soc., **46**, 1786 and 1810 (1924).

The alkaline solution is fairly stable in the absence of platinum, which catalyzes the reaction.

Hydrazine is not formed in the reduction of nitric acid or nitrates and appears to play no part in the ordinary mechanism of such reductions. It is said, however, to be formed in the reduction of the sulfite-nitric oxide complex, $K_2SO_3 \cdot 2NO$, by sodium amalgam; and Brackel[12] has described the reduction of $Ag_2N_2O_2$ with $KHSO_4$ to form hydrazine.

Nitrite to ammonia in alkaline solution. There is abundant evidence that the ordinary course of the reduction of nitrite in alkaline solution goes through the oxidation states, +1, −1, to −3, and the products under various conditions are hyponitrite, hydroxylamine, and ammonia. The potential values for the corresponding couples have been summarized in Table 19 (see p. 95). It will be observed that the greatest potential to be overcome in the reduction is for the +1 to −1 step, while in the oxidation of ammonia, the −3 to −1 step provides the highest barrier. The following experimental facts are of interest.

The cathodic reduction of concentrated nitrite with a mercury cathode described by Zorn[13] yields hyponitrite. The product may also be obtained by the reduction with sodium amalgam. It would appear that the union of two nitroxyls to form hyponitrous acid occurs less readily than the union of two NO^- ions to form $N_2O_2^{--}$, as hyponitrite is not readily formed in acid reduction. Hydroxylamine may be oxidized to hyponitrite by mercuric oxide (Hg-HgO, $E^\circ = -0.1$). The presence of mercury thus seems very definitely to favor the formation of hyponitrite in alkaline solution, although it is not to be implied that hyponitrite cannot be formed in its absence.

Although the cathodic reduction of nitrates in neutral or alkaline solution yields ammonia and no hydroxylamine, the reduction of nitrites on various cathodes gives a mixture of ammonia and hydroxylamine, according to the results of Suler.[14] The absence of hydroxylamine in the nitrate electrolysis must mean that nitrate is able to catalyze the reduction of hydroxylamine to ammonia in alkaline solutions. In view of the potentials, it is surprising that the reduction ever stops at hydroxylamine, but this slowness as an oxidizing agent in alkaline solutions is in line with its similar behavior in acid solutions. Baudisch and Mayer[15] report that ferrous hydroxide reduces nitrite quantitatively to ammonia in slightly alkaline solutions when a threefold excess of the reducing agent is used. Without the excess some nitrous oxide is formed.

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[12] Brackel, F., Ber., **33**, 2115 (1900).

[13] Zorn, W., Ber., **12**, 1509 (1879).

[14] Suler, B., Z. Elektrochem., **7**, 831 (1901).

Ammonium hydroxide is readily oxidized on various metal anodes to nitrite, and at high hydroxide concentration the oxidation does not go on to nitrate, as mentioned above. The presence of certain negative ions often leads to the formation of some nitrogen and nitrous oxide. Thus, Fichter[16] reports that the addition of ammonium carbonate to an ammonium hydroxide electrolyte with a platinum anode changes the oxidation product from nitrate to largely nitrogen and nitrous oxide.

The reduction of nitric and nitrous oxides. The inertness of nitric oxide in acid toward reduction by ferrous and titanous ions has been mentioned. It is, however, reduced by stannous to hydroxylamine and nitrogen and by stannite in alkali to hyponitrite, according to Divers and Haga.[17]

Nichols and Derbigny[18] have studied the reduction of nitrous oxide by various reagents in acid solution. They report the reduction by Ti^{+++} to ammonia, by Sn^{++} to hydroxylamine, and by H_2SO_3 (slowly) to nitrogen. It is interesting to note the reduction by titanous in view of the fact that it does not react with nitric oxide.

Hydrazoic acid. From Table 17 (p. 83), the free energy of hydrazoic acid, HN_3, is 65,300 cal. The acid is said to be slightly stronger than acetic acid. With 10^{-4} as the constant, the free energy of the ion N_3^- is found to be 70,750 cal. For the free energy of formation from hydrazine and nitrous acid, one calculates,

$$N_2H_4 + HNO_2 = HN_3 + 2H_2O, \qquad \Delta F^\circ = -64{,}860 \text{ cal.}$$

The potential for the ammonium ion–hydrazoic acid couple is,

$$3NH_4^+ = HN_3 + 11H^+ + 8e^-, \qquad E^\circ = -0.66.$$

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[15] Baudisch, O., and Mayer, P., Biochem. Zeit., **107**, 1 (1920).

[16] Fichter, F., Z. Elektrochem., **18**, 647 (1912).

[17] Divers, E., and Haga, T., Chem. News, **78**, 313 (1898).

[18] Nichols, M. L., and Derbigny, I. A., J. Phys. Chem., **30**, 491 (1926).

TABLE 18

SUMMARY OF POTENTIAL VALUES FOR THE NITROGEN COUPLES IN ACID SOLUTION

($E°$ in volts for the half-reactions relating each pair of substances.)

	NO_3^-	N_2O_4	HNO_2	NO	N_2O	$H_2N_2O_2$	N_2	NH_3OH^+	$N_2H_5^+$
N_2O_4	−0.81								
HNO_2	−0.94	−1.07							
NO	−0.96	−1.03	−0.99						
N_2O	−1.11	−1.21	−1.29	−1.59					
$H_2N_2O_2$	−0.87	−0.88	−0.80	−0.60					
N_2	−1.24	−1.35	−1.44	−1.68	−1.77	−2.75			
NH_3OH^+	−0.73	−0.71	−0.62	−0.50	0.05	−0.44	1.87		
$N_2H_5^+$	−0.84	−0.81	−0.79	−0.74	−0.46	−0.78	0.17	−1.48	
NH_4^+	−0.87	−0.89	−0.86	−0.84	−0.65	−0.87	−0.27	−1.35	−1.22

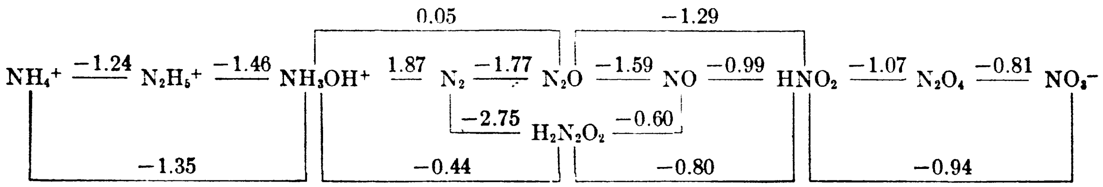
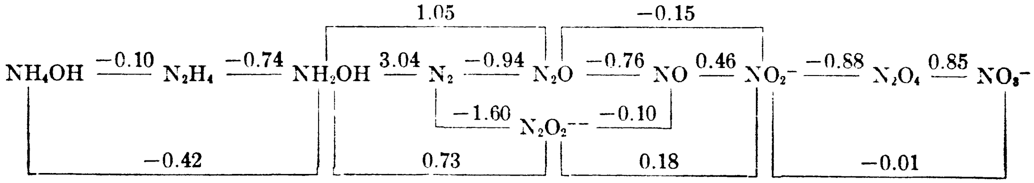


TABLE 19

SUMMARY OF POTENTIAL VALUES FOR THE NITROGEN COUPLES IN ALKALINE SOLUTION

(E°_B in volts for half-reactions relating each pair of substances.)

	NO_3^-	N_2O_4	NO_2^-	NO	N_2O	$N_2O_2^{--}$	N_2	NH_2OH	N_2H_4
N_2O_4	0.85								
NO_2^-	−0.01	−0.88							
NO	0.14	−0.21	0.46						
N_2O	−0.10	−0.38	−0.15	−0.76					
$N_2O_2^{--}$	0.08	−0.17	0.18	−0.10					
N_2	−0.24	−0.52	−0.41	−0.85	−0.94	−1.60			
NH_2OH	0.30	0.19	0.45	0.43	1.05	0.73	3.04		
N_2H_4	0.13	0.03	0.21	0.12	0.40	0.24	1.15	−0.74	
NH_4OH	0.10	0.01	0.15	0.10	0.25	0.15	0.74	−0.42	−0.10



Curtis and Darapsky[19] report the reduction of hydrazoic acid to ammonia by metals ranging from Al to Cu in reducing power. However, hydrazoic acid is a very much more powerful oxidizing agent in its reduction to nitrogen and ammonium.

$$NH_4^+ + N_2 = HN_3 + 3H^+ + 2e^-, \qquad E^\circ = -1.82$$

The oxidation of chloride to chlorine by this couple is reported by Browne and Hoel.[20]

Cook[21] has studied the reduction by sodium amalgam and ferrous hydroxide. Under these conditions he found the products to be hydrazine and ammonia.

$$7OH^- + N_2H_4 + NH_3 = N_3^- + 7H_2O + 6e^-, \qquad E_B^\circ = 0.62$$

Hydrazoic acid is also a powerful reducing agent.

$$HN_3 = \tfrac{3}{2}N_2 + H^+ + e^-, \qquad E^\circ = 2.8$$

$$N_3^- = \tfrac{3}{2}N_2 + e^-, \qquad E_B^\circ = 3.1$$

Sommer and Pincas[22] have studied the oxidation of hydrazoic acid with ceric ion and found it quantitative in the oxidation to nitrogen. The oxidation by iodine is also quantitative if a trace of thiosulfate is present, and Raschig has discussed possible mechanism of the thiosulfate action.

From the potentials given, it is obvious that hydrazoic acid is unstable with respect to its decomposition into nitrogen and ammonia. The free energy of the reaction is very large.

$$3HN_3 = 4N_2 + NH_3, \qquad \Delta F^\circ = -202 \text{ kcal.}$$

The catalysis by platinum has been studied by Oliveri-Mandala.[23]

Nitrosyl chloride and nitrosyl bromide. Lewis and Randall[24] calculate 16,010 cal. for the free energy of formation of nitrosyl chloride gas from equilibrium data on the reaction between nitric oxide and chlorine. From thermal and spectroscopic data the value would appear to be 15,960 cal., but as the difference is not large, the Lewis and Randall value will be used.

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[19] Curtis, T., and Darapsky, A., J. prakt. Chem., **61**, 408 (1900).

[20] Browne, A. W., and Hoel, A. B., J. Am. Chem. Soc. **44**, 2117 (1922).

[21] Cook, W. T., Proc. Chem. Soc., **19**, 213 (1904).

[22] Sommer, F., and Pincas, H., Ber., **49**, 259 (1916).

[23] Oliveri-Mandala, E., Gazz. chim. Ital., **46**, 137 and 298 (1916).

[24] Lewis, G. N., and Randall, M., *Thermodynamics* (McGraw-Hill, New York, 1923), p. 562. Compare Jahn, F. P., J. Chem. Phys. **6**, 338 (1938).

Blair, Brass, and Yost[25] found from the nitric oxide-bromine reaction that the free energy of formation of nitrosyl bromide gas is 19,260 cal.

With water, the chloride and bromide rapidly hydrolyze,

$$NOCl(g) + H_2O = HNO_2 + H^+ + Cl^-, \qquad \Delta F^\circ = -3685$$

$$NOBr(g) + H_2O = HNO_2 + H^+ + Br^-, \qquad \Delta F^\circ = 40.$$

The free energies indicate that the hydrolysis is quite large, especially with the chloride. For this reason the behavior of solutions of these nitrosyl compounds as oxidizing and reducing agents will be essentially that of nitrous acid.

Summary of nitrogen potentials. The values for the potentials relating the various nitrogen oxidation states in acid and alkali have been summarized in Tables 18 and 19. Most of the important facts regarding these potentials have already been presented. The values for the reductions and oxidations to molecular nitrogen, although of little chemical significance, are interesting from the energy standpoint. With respect to N_2, nitric acid (+5 state) is the most stable of the positive states and ammonium (−3 state) is the most stable of the negative states. On either side, the stability decreases rapidly and regularly from the high state to the low. In spite of the very favorable energy relations, only in the case of hydrazine is it possible to go quantitatively to nitrogen. For this case the explanation may be offered that the two nitrogens are already attached to each other and the reaction does not therefore have to proceed through atomic nitrogen with the resulting potential barrier. But such an explanation makes the case of hyponitrous acid particularly puzzling, for here, too, the nitrogens are presumably attached to each other, and yet with a potential almost equal to fluorine the reduction to N_2 does not occur.

Phosphorus

The standard state of phosphorus is the solid red (violet when pure) modification. All free energies will be referred to this state, although Bichowsky and Rossini have given their heats of formation in terms of the "white" solid. The entropy of red phosphorus is not known but it certainly lies between that of silicon and sulfur, as the compressibility shows this same relation. The value 7.0 cal. per degree will be used for this entropy. The heats and entropies of formation then lead to the following free energies for the various forms of the element: P(white, s), 1800 cal.; P_4(g), 13,100 cal.; P_2(g), 19,500 cal.; and P(g), 26,000 cal.

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[25] Blair, C. M., Brass, P. D., and Yost, D. M., J. Am. Chem. Soc., 56, 1916 (1934).

Oxidation states. The important compounds of the various oxidation states of phosphorus are: -3, phosphine, PH_3; -2, hydrogen diphosphide, P_2H_4; $+1$, hypophosphorous acid, H_3PO_2; $+3$, phosphorous acid, H_3PO_3 ; $+4$, hypophosphoric acid, $H_4P_2O_6$; and $+5$, orthophosphoric acid, H_3PO_4. The oxides P_2O_3, P_2O_4, and P_2O_5 exist, and claims are made for a suboxide, P_4O. The hydrogen phosphide, $(P_2H)_x$ —probably the tetraphosphide, P_4H_2—is fairly stable, and the compound PH, -1 state, is known as an unstable gas molecule. Halides of the $+2$, $+3$, and $+5$ oxidation states have been prepared.

The free energies of phosphorus compounds. Rapid reversible equilibrium is practically never attainable in oxidation-reduction reactions involving phosphorus or its compounds; hence, free energies are not available from equilibrium data. The entropies of phosphine and aqueous phosphoric acid and its ions are known. The value for orthophosphoric acid is 44.3 cal. per degree and the same value will be estimated for phosphorous and hypophosphorous acids. Ordinarily one less oxygen atom would be expected to decrease the entropy by several units, but this will probably be offset in these lower phosphorus acids by the shift of the hydrogens onto the phosphorus and a decrease in the entropy of hydration. The heats of formation of Bichowsky and Rossini have been corrected to red phosphorus by the transition heat 4.22 kcal. per gram atom.

The phosphorous-phosphoric acid couple. Pitzer[26] has chosen as the best values for the free energies of the three ionization steps of orthophosphoric acid: (1) 2898 cal., (2) 9830 cal., (3) 16,300 cal. The corresponding constants are: $K_1 = 7.5 \times 10^{-3}$; $K_2 = 6.2 \times 10^{-8}$; and $K_3 = 10^{-12}$. The free energies of the ionization steps, combining with the free energy of the acid (see Table 20), yield the following free energies: $H_2PO_4^-$, $-267,100$ cal.; HPO_4^{--}, $-257,270$ cal.; PO_4^{---}, $-240,970$ cal.

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[26] Pitzer, K. S., J. Am. Chem. Soc., **59**, 2365 (1937).

Kolthoff[27] found for phosphorous acid, $K_1 = 0.016$ and $K_2 = 7 \times 10^{-7}$. For the free energies of the ions, one then calculates, $H_2PO_3^-$, −201,550 cal. and HPO_3^{--}, −193,150 cal. The evidence is fairly conclusive that the third hydrogen is attached to the phosphorus and is not replaceable.

These values lead to the following potentials for the phosphorous-phosphoric acid couple.

$$H_2O + H_3PO_3 = H_3PO_4 + 2H^+ + 2e^-, \qquad E^\circ = 0.20$$

$$3OH^- + HPO_3^{--} = PO_4^{---} + 2H_2O + 2e^-, \qquad E_B^\circ = 1.05$$

The mechanism of the couples is discussed under hypophosphoric acid.

TABLE 20
THERMAL DATA USED FOR THE CALCULATION OF THE FREE ENERGIES OF FORMATION

Compound	ΔH°	ΔS°	ΔF°
$H_3PO_4(aq)$	−302,000	−108	−270,000
$H_3PO_3(aq)$	−228,600	(−83)	−204,000
$H_3PO_2(aq)$	−137,200	(−59)	−120,000
$PH_3(aq)$	1,900	−3.3	2,880
$P_4H_2(s)$	6,900	(−31)	16,000

The ΔH° of the reaction of metaphosphoric acid with water to form the ortho-acid is given as 3150 cal. The entropy change is probably also small; hence, the potentials of the above couples, or at least the couple in acid solution, is probably not much different for the meta-acid. The thermal data would indicate that the pyrophosphoric acid was several tenths of a volt better oxidizing agent than the ortho-acid.

Hypophosphoric acid. There are no data available for the calculation of the free energy of hypophosphoric acid, $H_4P_2O_6$ (or H_2PO_3). However the reaction

$$H_4P_2O_6 + H_2O = H_3PO_3 + H_3PO_4,$$

although slow in cold dilute solutions, goes if the solution is concentrated and somewhat acid. Considerable heat appears to be evolved. If we assume −30 kcal. as the free energy of the reaction, this would make the free energy of hypophosphoric acid, $H_4P_2O_6$, −390 kcal. and would give the following potentials:

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[27] Kolthoff, I. M., Rec. trav. chim., Pays-Bas, **46**, 350 (1927).

$$2H_2O + H_4P_2O_6 = 2H_3PO_4 + 2H^+ + 2e^-, \qquad E^\circ = (0.8)$$

$$2H_3PO_3 = H_4P_2O_6 + 2H^+ + 2e^-, \qquad E^\circ = (-0.4).$$

These potentials are certainly approximately correct and throw considerable light on the problem of the phosphorous-phosphoric acid couple. Even a very powerful one-electron reducing agent, such as titanous ion, would be unable to reduce phosphate in acid solution to H_2PO_3. On the other hand, a fairly powerful one-electron oxidizing agent would be required to oxidize phosphorous acid to H_2PO_3. The reaction should not stop there; but, because of the ease of the next step, the H_2PO_3 should be oxidized to phosphoric acid. The assumptions appear to agree with the experimental facts. Linhart[28] found that the reaction of phosphorous acid with mercuric chloride formed mercurous chloride, and the reaction was monomolecular with respect to the mercuric chloride. This first step of the reaction was slow and appeared to be followed by a rapid step giving phosphoric acid. It seems strange, however, that there is not some mechanism by which phosphoric acid can go directly to the phosphorous acid by the shift of an oxygen as, for example, in the reduction of nitric acid by sulfite. The answer probably is that no such reducing agent exists with a potential as low as the 0.2 required for the two-electron step.

Hypophosphorous acid. Kolthoff[29] records 0.01 as the dissociation constant of hypophosphorous acid. Only one of the hydrogens is replaceable, indicating that the other two are attached directly to the phosphorus. From this constant the free energy of $H_2PO_2^-$ is −117,300 cal., and the potentials for the couples relating the acid to higher and lower oxidation states are,

$$H_2O + H_3PO_2 = H_3PO_3 + 2H^+ + 2e^-, \qquad E^\circ = 0.59$$

$$3OH^- + H_2PO_2^- = HPO_3^{--} + 2H_2O + 2e^-, \qquad E^\circ_B = 1.65$$

$$2H_2O + P = H_3PO_2 + H^+ + e^-, \qquad E^\circ = 0.29$$

$$2OH^- + P = H_2PO_2^- + e^-, \qquad E^\circ_B = 1.82.$$

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[28] Linhart, G. A., Am. J. Sci. (4), **35**, 353 (1913).
[29] Kolthoff, I. M., Rec. trav. chim., **46**, 350 (1927).

Hypophosphorous acid is thus a very weak oxidizing agent and a very powerful reducing agent in both acid and basic solutions. A number of important decomposition reactions are considered in a later paragraph.

Phosphine and other hydrogen phosphides. The solubility of phosphine in water is about 0.01 *M* as given by Stock, Böttcher, and Lenger.[30] This would make the free energy of solution 2730 cal. The free energy of dissociation of phosphonium ion into phosphine and hydrogen ion must be close to zero, as the solution of the gas is not alkaline. One can then estimate the free energy of phosphonium ion; but, as it is unstable with respect to the phosphine gas, it will be simpler in writing all half-reactions in acid solution involving phosphine to use $PH_3(g)$. From the free energies derived above, one calculates,

$$PH_3(g) = P + 3H^+ + 3e^-, \qquad E^\circ = 0.04$$

$$3OH^- + PH_3(g) = P + 3H_2O + 3e^-, \qquad E^\circ_B = 0.87$$

and similarly for the tetraphosphide,

$$P_4H_2 = 4P + 2H^+ + 2e^-, \qquad E^\circ = 0.35$$

$$2OH^- + P_4H_2 = 4P + 2H_2O + 2e^-, \qquad E^\circ_B = 1.18.$$

The energy thus favors the formation of phosphine over the formation of the tetraphosphide in the reduction of phosphorus. The data are insufficient to calculate the free energy of the diphosphide, but the value must be fairly positive as indicated by the fact that the following reaction occurs quite readily at room temperature,

$$5P_2H_4(l) = 6PH_3(g) + P_4H_2(s).$$

Phosphorus halogen compounds. Yost and Anderson[31] found $-63{,}300$ cal. for the free energy of formation of phosphorus chloride $PCl_3(l)$ from chlorine and white phosphorus. With reference to red phosphorus, this becomes $-61{,}500$ cal. In cold water the chloride hydrolyzes to phosphorous acid,

$$PCl_3(l) + 3H_2O = H_3PO_3 + 3H^+ + 3Cl^-, \qquad \Delta F^\circ = -67 \text{ kcal.}$$

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[30] Stock, A., Böttcher, W., and Lenger, W., Ber., **42**, 2855 (1909).
[31] Yost, D. M., and Anderson, T. F., J. Chem. Phys., **2**, 624 (1934).

The free energies of a number of other halogen compounds may be estimated; but, because of their hydrolysis to the corresponding acids, their chemistry in water solutions is essentially that of the acids. However the solid diiodide, PI_2, is of interest since it is one of the few compounds of phosphorus having the +2 oxidation state. Its heat of formation is −5700 cal. and since all the substances are solids the entropy of formation may be taken as zero, and the free energy equal to the heat. The hydrolysis reaction is,

$$2PI_2(s) + 5H_2O = H_3PO_3 + H_3PO_2 + 4H^+ + 4I^-, \qquad \Delta F^\circ = -78 \text{ kcal.}$$

The potential for the P, I^--PI_2 couple would be about −0.1, but it is doubtless of little significance.

Summary of phosphorus potentials. The potential relations of the various phosphorus oxidation states are shown in the following schemes:

ACID SOLUTION

$$\begin{array}{ccccccccccccc} -3 & & -2 & & 0 & & +1 & & +3 & & +4 & & +5 \\ PH_3 & \overset{0.0}{\text{—}} & P_2H_4 & \overset{0.1}{\text{—}} & P & \overset{0.29}{\text{—}} & H_3PO_2 & \overset{0.59}{\text{—}} & H_3PO_3 & \overset{(-0.40)}{\text{——}} & H_2PO_3 & \overset{(0.80)}{\text{——}} & H_3PO_4 \end{array}$$

$$\underbrace{PH_3 \;\text{—}\; P}_{0.04} \qquad \underbrace{P \;\text{—}\; H_3PO_3}_{0.49} \qquad \underbrace{H_3PO_3 \;\text{—}\; H_3PO_4}_{0.20}$$

BASIC SOLUTION

$$\begin{array}{ccccccccccccc} -3 & & -2 & & 0 & & +1 & & +3 & & +4 & & +5 \\ PH_3 & \overset{0.8}{\text{—}} & P_2H_4 & \overset{0.9}{\text{—}} & P & \overset{1.82}{\text{—}} & H_2PO_2 & \overset{1.65}{\text{—}} & HPO_3^{--} & \text{——} & PO_3^{--} & \text{——} & PO_4^{---} \end{array}$$

$$\underbrace{PH_3 \;\text{—}\; P}_{0.87} \qquad \underbrace{P \;\text{—}\; HPO_3^{--}}_{1.71} \qquad \underbrace{HPO_3^{--} \;\text{—}\; PO_4^{---}}_{1.02}$$

The consideration of these potentials leads to a discussion of a number of important decomposition reactions.

Phosphorus is unstable with respect to its hydrolysis into the +1 and −3 states.

$$4P + 6H_2O = PH_3 + 3H_3PO_2, \quad \Delta F^\circ = -17.0 \text{ kcal.}$$

$$4P + 3OH^- + 3H_2O = 3H_2PO_2^- + PH_3, \quad \Delta F^\circ = -66.2 \text{ kcal.}$$

The free energy for the reaction in alkaline solution is large and the reaction goes very readily.

Because of the enormous reducing power of phosphorus in alkaline solution (1.82 volts), it also liberates some hydrogen along with the products of the above reaction,

$$2P + 2OH^- + 2H_2O = 2H_2PO_2^- + H_2, \quad \Delta F^\circ = -46.0 \text{ kcal.}$$

Hypophosphorous acid is unstable with respect to its decomposition into phosphorous acid and phosphine.

$$3H_3PO_2 = PH_3 + 2H_3PO_3, \quad \Delta F^\circ = -53.2 \text{ kcal.}$$

This reaction occurs readily, and because of strong reducing potential the acid will also reduce water.

$$H_3PO_2 + H_2O = H_3PO_3 + H_2, \quad \Delta F^\circ = -27.3 \text{ kcal.}$$

The decomposition of phosphorous acid into phosphine and phosphoric acid has a small positive free energy.

$$4H_3PO_3 = PH_3 + 3H_3PO_4, \quad \Delta F^\circ = 8.8 \text{ kcal.}$$

However, because of the volatility of the phosphine the equilibrium may be displaced upon heating, and the decomposition occurs in hot solutions.

It is obvious also that, through these various steps, phosphorus is unstable with respect to its hydrolysis into the +5 and −3 oxidation states.

The most remarkable characteristic of the phosphorus potentials is their highly positive value. Even weak oxidation agents will oxidize phosphine all the way up to phosphorous acid, and from the overall potentials these agents should take this acid up to phosphoric. Actually, oxidizing agents of about the strength of iodine are required for this last step, which seems to indicate that the mechanism is through the hypophosphoric acid as discussed above.

Arsenic

The standard state of arsenic is the solid metallic form, As α. There is also a yellow, cubic, low density form, As γ, and an amorphous form, As β. There are not enough reliable data to calculate the free energies of these modifications and they are relatively unimportant. From the heats and entropies of formation, the free energy of the monatomic gas, As(g), is 20.4 kcal. and of the tetra- molecule, $As_4(g)$, 20.5 kcal.

Oxidation states. The important oxidation states of arsenic are: −3 in arsine, +3 in arsenious acid, and +5 in arsenic acid. The hydrogen arsenide, As_2H_2, −1, may be prepared. Very few definite compounds of the even oxidation states exist: the oxide As_2O_4 appears to be a compound of the +3 and +5 oxides, but the monosulfide AsS (+2) is a well-known mineral.

Arsine. Estimating the entropy of arsine as 52 in comparison to 50.35 for phosphine and using Ogier's value[32] of 36.7 kcal. for the heat of formation, we find the free energy of arsine gas, $AsH_3(g)$, to be 37.7 kcal. In view of the slightly lower value for stibine, it is quite likely that this value for arsine is too high. But in the absence of definite evidence regarding the discrepancy, it will be used. The potentials of the arsine-arsenic couples are:

$$AsH_3 = As + 3H^+ + 3e^-, \qquad E^\circ = 0.54$$

$$3OH^- + AsH_3 = As + 3H_2O + 3e^-, \qquad E^\circ_B \doteq 1.37.$$

Arsine is thus a powerful reducing agent and should be readily oxidized by moderately strong oxidizing agents; the oxidation by hydrogen ion however is not rapid.

A metallic arsenic cathode may be reduced to arsine, especially in alkaline solutions, according to the results of Grube and Kleber,[33] and arsenious acid is reduced to arsine efficiently at a mercury cathode (cf. work by Aumonier[34]).

It is claimed that the reduction of arsenic trichloride by stannous chloride yields the solid phosphide, As_2H_2, which is unstable with respect to the decomposition into the elements. No data are available by which its free energy may be estimated.

The arsenic-arsenious acid couple. Schuhmann[35] has measured the electromotive force of the cell for which the net reaction is,

$$As_2O_3(s) + 3H_2 = 2As + 3H_2O.$$

His result gives for the couple,

$$3H_2O + 2As = As_2O_3 + 6H^+ + 6e^-, \qquad E^\circ = -0.2340.$$

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[32] Ogier, J., Comp. rend., **87**, 210 (1878).

[33] Grube, G., and Kleber, H., Z. Elektrochem., **30**, 517 (1924).

[34] Aumonier, F. S., J. Soc. Chem. Ind., **46**, 341 (1927).

[35] Schuhmann, R., J. Am. Chem. Soc., **46**, 1444 (1924).

Arsenious oxide is slowly soluble to form the acid, $HAsO_2$, or some hydrate of this acid, and the molality of the saturated solution is 0.2067 at 25° C. Schuhmann has calculated the free energy of solution and, correcting a missprint in his value, one obtains,

$$2H_2O + As = HAsO_2(aq) + 3H^+ + 3e^-, \quad E^\circ = -0.2475.$$

The corresponding free energies are: $As_2O_3(s)$, −137,670 cal.; $HAsO_2(aq)$, −96,345 cal.; and $H_3AsO_3(aq)$, −153,035 cal. The more recent data on the dissociation of arsenious acid are fairly consistent. Hughes[36] from glass electrode measurements reported,

$$HAsO_2 = H^+ + AsO_2^-, \qquad K = 6 \times 10^{-10}.$$

Britton and Jackson[37] are in agreement. Based on this value, the free energy of AsO_2^- is −83,770 cal., and the potential of the couple in alkaline solution is,

$$4OH^- + As = AsO_2^- + 2H_2O + 3e^-, \qquad E^\circ_B = 0.68.$$

From the values of these couples it is apparent that arsenic is a seminoble metal.

Randall's[38] recalculation of the data by Washburn gives for the basic dissociation constant of arsenious acid,

$$HAsO_2 = AsO^+ + OH^-, \qquad K = 5.0 \times 10^{-15}.$$

It is obvious from this value that the concentration of AsO^+ is not large except in high acid. The free energy of AsO^+ is −39,260 cal.

The arsenious acid–arsenic acid couple. Liebhafsky[39] has reviewed the data of Roebuck on the equilibrium established in the oxidation of arsenious acid by triiodide. His value for the constant is,

$$\frac{(H_3AsO_4)\,(H^+)^2\,(I^-)^3}{(I_3^-)\,(H_3AsO_3)} = 1.6 \times 10^{-1}.$$

The corresponding free energy of the reaction is 1085 cal. and the free energy of the arsenic acid, $H_3AsO_4(aq)$, −183,930 cal. Washburn[40] gives the approximate values for the three dissociation constants as $K_1 = 4.8 \times 10^{-3}$, $K_2 = 10^{-7}$, and $K_3 = 10^{-13}$, from which one calculates the free energies, $H_2AsO_4^-$, $-180{,}700$ cal.; $HAsO_4^{--}$, $-171{,}100$ cal.; and AsO_4^{---}, $-153{,}400$ cal. The potentials of the following couples may then be calculated:

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[36] Hughes, W. S., J. Chem. Soc., 491 (1928).

[37] Britton, H. T. S., and Jackson, P., J. Chem. Soc., 1048 (1934).

[38] Randall, M., International Critical Tables, VII, 242.

[39] Liebhafsky, H. A., J. Phys. Chem., **35**, 1648 (1931).

$$2H_2O + HAsO_2 = H_3AsO_4 + 2H^+ + 2e^-, \qquad E^\circ = -0.559$$

$$4OH^- + AsO_2^- = AsO_4^{---} + 2H_2O + 2e^-, \qquad E^\circ_B = 0.71.$$

The couple is capable of attaining a rapid reversible equilibrium and the mechanism of the oxidation of arsenite by iodine appears to be that of a direct oxygen shift through the medium of hypoiodous acid,

$$H_3AsO_3 + HIO = H_3AsO_4 + H^+ + I^-.$$

Arsenic sulfides. The chemistry of arsenious sulfide, As_2S_3, and arsenic sulfide, As_2S_5, and their acid ions, thioarsenite, AsS_2^- and thioarsenate, AsS_4^{---}, is of importance in analytical work. The only thermal data relating to the problem is the heat of formation of the arsenious sulfide, -20 kcal. The entropy of formation must be small, as all the substances are solids; hence this value may also be taken as an approximation for the free energy of formation. For the precipitation of the sulfide, one calculates,

$$3H_2S + 2HAsO_2(aq) = 4H_2O + As_2S_3, \qquad \Delta F^\circ = -30{,}500 \text{ cal.}$$

The following reactions relate this free energy to that of the ion AsS_2^-.

$$2As_2S_3 + 4OH^- = 3AsS_2^- + AsO_2^- + 2H_2O$$

$$As_2S_3 + S^{--} = 2AsS_2^-$$

$$2AsS_2^- + 2H^+ = As_2S_3 + H_2S$$

The difference in free energy of the last two reactions is the free energy of ionization of hydrogen sulfide, 31 kcal. Assuming that the two reactions go with about equal readiness, the free energy of AsS_2^- would be -6 kcal. Hence,

$$2S^{--} + As = AsS_2^- + 3e^-, \qquad E^\circ_B = \text{ca } 0.75$$

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[40] Washburn, E. W., J. Am. Chem. Soc., **30**, 31 (1908).

The +3 sulfide is oxidized to thioarsenate by polysulfide. From the potential of S_2^{--} one can state,

$$2S^{--} + AsS_2^{--} = AsS_4^{---} + 2e^-, \qquad E^\circ_B > 0.6$$

Arsenic trichloride. Yost and Anderson[41] report −65,190 cal. as the free energy of liquid trichloride, $AsCl_3$. The free energy of its hydrolysis reaction is,

$$AsCl_3(l) + 2H_2O = HAsO_2 + 3H^+ + 3Cl^-, \qquad \Delta F^\circ = -11.8 \text{ kcal.}$$

The value for this energy is considerably lower than that for the corresponding phosphorus reaction. Thomsen[42] records −17.6 kcal. for the heat of the reaction; and this, together with the free energy of the reaction and entropies of the other substances, gives 29.1 cal. per degree for the entropy of $HAsO_2(aq)$ which appears to be a very reasonable figure. The trichloride dissolves in concentrated hydrochloric acid, probably with the formation of the complex ion $AsCl_4^-$.

Summary of arsenic potentials. For convenience the principal arsenic potentials are summarized in the following scheme:

ACID SOLUTION

$$AsH_3 \xrightarrow{0.54} As \xrightarrow{-0.2475} HAsO_2 \xrightarrow{-0.559} H_3AsO_4$$

BASIC SOLUTION

$$AsH_3 \xrightarrow{1.37} As \xrightarrow{0.68} AsO_2^- \xrightarrow{0.71} AsO_4^{---}$$

There is not much to add to the discussion of these potentials given above, but it may be pointed out that arsenic, unlike phosphorus, will not hydrolyze to give the +3 and −3 states,

$$4As + 3H_2O = As_2O_3 + 2AsH_3, \qquad \Delta F^\circ = 108 \text{ kcal.}$$

Antimony

The standard state of antimony is the solid metallic trigonal form. The heat of transition of the unstable "explosive" modification is given as −2.32 kcal., but the entropy of this form is not known, so the free energy cannot be calculated. From thermal data one finds the free energy of the monatomic gas, Sb(g), to be 44 kcal. and the diatomic gas, $Sb_2(g)$, to be 40 kcal.

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[41] Yost, D. M., and Anderson, T. F., J. Chem. Phys., **2**, 624 (1934).

[42] Thomsen, J., *Thermochemische Untersuchungen* (Barth, Leipzig, 1886).

Oxidation states. The principal oxidation states are −3 in SbH_3, + 3 in Sb_2O_3, and +5 in Sb_2O_5. The +4 oxide Sb_2O_4 is quite stable, and claims are made for existence of the corresponding hypoantimonic acid, $H_2Sb_2O_5$.

The stibine-antimony couple. The value given by Stock and Wrede[43] for the heat of formation of stibine, 34.0 kcal., appears to be reliable, although the older value of Berthelot and Petit is 2½ times larger. The behavior of stibine and arsine upon heating certainly indicates that the latter is the more stable, and it may be that the Stock and Wrede value for stibine, which is less than the accepted value for arsine, is a little too low, but this inconsistency probably lies in the heat of formation of arsine. However, calculations will be made using this heat of formation. Estimating the entropy of stibine as 53 cal. per degree, in comparison with 50.35 for phosphine, the free energy of stibine is 35.3 kcal. Sand and his co-workers[44] found 37.1 at 20° C. from cathodic reduction potentials. For the stibine-antimony couple in acid solution, one computes,

$$SbH_3(g) = Sb + 3H^+ + 3e^-, \qquad E^\circ = 0.51$$

Assuming no acid character for stibine, the potential for the couple in basic solution would be $E^\circ_B = 1.34$. However, since stibine appears to form the sodium salt Na_3Sb in concentrated alkali, the calculated basic potential would be too large. $E^\circ_B < 1.34$. Because of this distinctly acid property of stibine and of the insolubility of many of the antimonides, a number of positive ions which would otherwise oxidize stibine form the antimonide, for example, Ag^+ forms Ag_3Sb.

The antimony-antimonous acid couple. Schuhmann[45] has measured the electromotive force of the cell having the net reaction,

$$Sb_2O_3(s) + 3H_2 = 2Sb + 3H_2O$$

and gives

$$3H_2O + 2Sb = Sb_2O_3 + 6H^+ + 6e^-, \qquad E^\circ = -0.152.$$

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[43] Stock, A., and Wrede, F., Ber., **40**, 2923 (1907).

[44] Sand, H. J. S., Weeks, E. J., and Worrell, S. W., J. Chem. Soc., **123**, 456 (1923).

[45] Schuhmann, R., J. Am. Chem. Soc., **46**, 52 (1924).

He has also measured this solubility and found for concentrations in the neighborhood of .1 *M* that the positive ion in solution is SbO^+. For the antimony-antimonyl couple he records,

$$Sb + H_2O = SbO^+ + 2H^+ + 3e^-, \qquad E^\circ = -0.212.$$

The corresponding free energies are, Sb_2O_3, $-149{,}030$ cal. and SbO^+, $-42{,}000$ cal. For the basic dissociation of the oxide, one calculates,

$$\tfrac{1}{2}Sb_2O_3 + \tfrac{1}{2}H_2O = SbO^+ + OH^-, \qquad K = 10^{-17}.$$

The solubility of the sesquioxide is given as 0.016 g per liter at 15° C. by Schulze.[46] This would lead to a free energy of ca $-97{,}500$ cal. for $HSbO_2(aq)$. The acid dissociation has not been determined, but from the concentration of hydroxide required to prevent the hydrolysis of SbO_2^-, a value of $K = 10^{-11}$ would appear to be a close approximation. Hence,

$$HSbO_2(aq) = H^+ + SbO_2^-, \qquad \Delta F^\circ = 15{,}000$$

and the free energy of SbO_2^- would be $-82{,}500$ cal.

$$4OH^- + Sb = SbO_2^- + 2H_2O + 3e^-, \qquad E_B^\circ = 0.66$$

Grube and Schweigardt[47] report 0.675 for this potential from cell measurements in 10*M* KOH. The metal may be precipitated by cathodic reduction in either acid or alkaline solution.

The antimonous-antimonic acid couple. From the Bichowsky and Rossini value for the heat of formation of the pentoxide, Sb_2O_5, $-230{,}000$ cal. and the entropy of formation, -115.6 cal. per degree, the free energy of the oxide appears to be $-195{,}500$ cal. Hence,

$$2H_2O + Sb_2O_3 = Sb_2O_5 + 4H^+ + 4e^-, \quad E^\circ = -0.73$$

$$3H_2O + 2SbO^+ = Sb_2O_5 + 6H^+ + 4e^-, \quad E^\circ = -0.64.$$

Pauling[48] has summarized the evidence in favor of the formula $HSb(OH)_6$ for orthoantimonic acid. The free energy of this acid or the solubility of the oxide in water is not known. Likewise, the acid dissociation constants have not been determined, although the solutions of the oxide are known to be fairly acid. Grube and Schweigardt[49] report from cell measurements in 10 M KOH,

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[46] Schulze, H., J. prakt. Chem., **27**, 320 (1883).

[47] Grube, G., and Schweigardt, F., Z. Elektrochem., **29**, 257 (1923).

[48] Pauling, L., J. Am. Chem. Soc., **55**, 1895 (1933).

$$SbO_2^- + 2OH^- (10M) = SbO_3^- + H_2O + 2e^-, \quad E^\circ = 0.589.$$

There is, however, no evidence that the +5 antimony is present as the meta-ion SbO_3^-, and the half-reaction might well be,

$$SbO_2^- + 5OH^- = H_3SbO_6^{-4} + H_2O + 2e^-.$$

In the latter case the correction for the hydroxide activity would be considerably larger and the E° value would probably be around 0.40.

The couple is capable of attaining rapid equilibrium in both acid and basic solutions. Antimonic acid will oxidize iodide but the reaction is reversed in alkaline solution. In the analytical methods using this reaction, tartrate is added to aid in keeping the +3 antimony in solution.

Antimony tetroxide. The data of Mixter[50] on the heat of formation of the oxide Sb_2O_4 is incompatible with its chemical properties. Using the value of Simon and Thaler,[51] −193,300 cal., and the entropy of formation −91.7 cal. per degree, the free energy is found to be −165,900 cal.

$$H_2O + Sb_2O_4 = Sb_2O_5 + 2H^+ + 2e^-, \quad E^\circ = -0.59$$

$$2H_2O + 2SbO^+ = Sb_2O_4 + 4H^+ + 2e^-, \quad E^\circ = -0.68$$

The oxide in acid is thus unstable with respect to the +3 and +5 oxidation states; the decomposition is slow in acid but more rapid in alkaline. Strong hydroxides dissolve the oxide but there are no data for the free energies.

Antimony trichloride. From the heat of formation, −91,400 cal., and the entropy of formation, −45.7 cal. per degree, one finds the free energy of antimony trichloride, $SbCl_3(s)$, to be −77,800 cal. For the hydrolysis to antimonyl ion, one calculates from this free energy,

$$SbCl_2(s) + H_2O = SbO^+ + 2H^+ + 3Cl^-, \quad \Delta F^\circ = -1500 \text{ cal.}$$

However, the reaction is complicated by the formation, at low hydrogen ion, of the solid basic chloride, $Sb_4O_5Cl_2$, and at high hydrochloric acid concentration of the complex chlorides $SbCl_4^-$ and $SbCl_6^{---}$. The free energies of the reactions to form these complex chlorides cannot be calculated from the present data.

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[49] Grube, G., and Schweigardt, F., Z. Elektrochem., **29**, 257 (1923).
[50] Mixter, W. G., Am. J. Sci., **28**, 103 (1909).
[51] Simon, A., and Thaler, E., Z. anorg. allgem. Chem., **162**, 253 (1927).

The pentachloride, $SbCl_5$, is more highly hydrolyzed than the trichloride and forms the solid oxide, Sb_2O_5, with some of the acid, $HSb(OH)_6$, in solution.

The antimony sulfides. The heat of formation of the orange precipitated antimonous sulfide, Sb_2S_3, may be taken equal to the free energy of formation, as a close approximation, since all the substances are solids, hence $\Delta F^\circ = -35{,}700$ cal.

$$2SbO^+ + 3H_2S(g) = Sb_2S_3 + 2H_2O + 2H^+, \qquad \Delta F^\circ = -41 \text{ kcal.}$$

This free energy seems too large in view of the reversal of the equilibrium in concentrated HCl. However, the formation of the complex chlorides may be sufficient to account for it. The sulfide is soluble in sulfide ion,

$$Sb_2S_3 + S^{--} = 2SbS_2^-,$$

and the reaction is reversed in dilute acid solutions. From the equilibrium, the value $-13{,}000$ cal. may be taken as a rough estimate of the free energy of the thioantimonite ion SbS_2^-. The electrolytic reduction of the thioantimonite is employed in the quantitative estimation of antimony (cf. Treadwell and Hall[52]).

$$Sb + 2S^{--} = SbS_2^{--} + 3e^-, \qquad E^\circ = \text{ca } 0.85$$

This E° value is in agreement with the fact that the metal is oxidized to the thioantimonite by polysulfide, S_2^{--}, which hasa potential of about 0.5.

There are no free energy data on the antimonic sulfide, Sb_2S_5. It is soluble in sulfide ion to form the thioantimonate, and, in acid, hydrogen sulfide reduces it to the antimonous sulfide. In alkaline solution thioantimonite is oxidized to the thioantimonate by S_2^{--}, and hence,

$$2S^{--} + SbS_2^- = SbS_4^{---} + 2e^{--}, \qquad E^\circ > 0.6$$

Summary of antimony potentials. For convenience the potential relating the principal antimony oxidation states are summarized in the following scheme:

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[52] Treadwell, F. P., and Hall, W. T., *Analytical Chemistry* (Wiley, New York, 1935), II, 222.

ACID SOLUTION

$$SbH_3 \xrightarrow{-0.51} Sb \xrightarrow{-0.212} SbO^+ \xrightarrow{-0.64} Sb_2O_5(s)$$

BASIC SOLUTION

$$SbH_3 \xrightarrow{<1.3} Sb \xrightarrow{0.66} SbO_2^- \xrightarrow{\text{ca } 0.40} H_3SbO_6^{---}$$

Bismuth

The standard state of bismuth is the solid metal. Accepting the Bichowsky and Rossini values for the heats of formation and combining with the entropies of formation, one finds the free energy of the monatomic gas, Bi(g), to be 38.5 kcal.

Oxidation states. The very unstable hydrogen compound BiH_3, -3 state, and also the hydride $Bi_2H_2(-1)$ have been prepared. Many bismuthides of the type Na_3Bi are known. The oxide and halides of the $+2$ oxidation state may be prepared. The most stable state is the $+3$ as represented by Bi_2O_3 and its compounds. The oxide $Bi_2O_5(+5)$ is a very powerful oxidizing agent as is also the tetroxide, $Bi_2O_4(+4)$, which is probably to be considered as bismuthyl bismuthate, $BiO \cdot BiO_3$.

Bismuth hydrogen compounds. Paneth[53] prepared bismuthine. He reports that at room temperature 80 per cent of the gas decomposed in 50 minutes and the decomposition was very rapid at 350° C. There are no other data to estimate its free energy; however, a stronger reducing agent than zinc must be used, for example, Mg, for the reduction of the metal.

$$BiH_3(g) = Bi + 3H^+ + 3e^-, \qquad E^\circ > 0.8$$

The bismuthine is acidic in properties and forms Ag_3Bi with silver nitrate. Weeks and Druce[54] have discussed the preparation of the solid hydride, Bi_2H_2. They found that, when heated in a vacuum, it decomposed according to the equation,

$$3Bi_2H_2 = 4Bi + 2BiH_3.$$

The bismuth-bismuthyl couple. Swift[55] and Smith[56] studied the ionic species in a solution of Bi_2O_3 in perchloric acid and concluded that at moderate hydrogen-ion concentration the ion is BiO^+ or $Bi(OH)_2^+$ and at higher concentrations $BiOH^+$. By the direct cell measurements the potential of the bismuth-bismuthyl couple is found to be around −0.31 to −0.32. The higher value will be used.

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[53] Paneth, F., Ber., **51**, 1704 and 1728 (1918).

[54] Weeks, E. J., and Druce, J. G. F., J. Chem. Soc., **127**, 1799 (1925).

[55] Swift, E. H., J. Am. Chem. Soc., **45**, 371 (1923).

[56] Smith, D. F., J. Am. Chem. Soc., **45**, 360 (1923).

$$H_2O + Bi = BiO^+ + 2H^+ + 3e^-, \qquad E^\circ = -0.32$$

This corresponds to a free energy of −34,550 cal. for BiO^+. From the heat of formation, −137,000 cal., and the entropy of formation, −68.5 cal. per degree, one finds the free energy of formation of the oxide, Bi_2O_3, to be −116,600 cal. The oxide is not appreciably soluble in cold 1 molal hydroxide. Hence

$$6OH^- + 2Bi = Bi_2O_3 + 3H_2O + 6e^-, \qquad E_B^\circ = 0.44$$

Baur and Lattmann[57] reported from direct cell measurements $E_B^\circ = 0.41$. However, the formation of the monoxide (vide infra) as an intermediate step may have entered into their determination.

Bismuthyl hydroxide, BiOOH, may be precipitated, and its solubility is recorded as 5.8×10^{-6} *M*. If one were justified in assuming complete ionization into hydroxide and bismuthyl ions, the solubility product would be 3.3×10^{-12}. From the free energies, one calculates,

$$\tfrac{1}{2}Bi_2O_3 + \tfrac{1}{2}H_2O = BiO^+ + OH^-, \qquad K = 2.3 \times 10^{-11}.$$

As the free energy of hydration of the oxide appears to be a small negative quantity, this calculation seems to substantiate the solubility products computed for the bismuthyl hydroxide, and we shall write,

$$BiOOH(s) = BiO^+ + OH^-, \qquad K = \text{ca } 1 \times 10^{-12}$$

Bismuth trichloride and oxychloride. The oxychloride is of such importance in the chemistry of +3 bismuth that its free energy relation will be considered at this point.

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[57] Baur, E., and Lattmann, W., Z. Elektrochem., **40**, 582 (1934).

Noyes and Chow[58] found for the reaction,

$$\tfrac{3}{2}H_2 + BiOCl(s) = Bi + H_2O + H^+ + Cl^-, \qquad E^\circ = 0.16$$

or

$$H_2O + Cl^- + Bi = BiOCl + 2H^+ + 3e^-, \quad E^\circ = -0.16$$

This corresponds to a free energy of −77,000 cal. for BiOCl. From the free energies we may calculate,

$$BiOCl = BiO^+ + Cl^-, \qquad \Delta F^\circ = 11{,}100 \text{ cal.}, \quad K = 7 \times 10^{-9}.$$

Considering the sensitivity of the oxychloride test for bismuth, this constant appears to be a little large. Feitknecht[59] calculated,

$$BiOCl + H_2O = Bi^{+++} + Cl^- + 2OH^-; \; K = 1.6 \times 10^{-31}.$$

However, there would seem to be some question about the validity of the determination of the concentration of Bi^{+++} upon which the constant is based.

Noyes, Hall, and Beattie[60] studied the solubility of the oxychloride in hydrochloric acid. For moderate concentrations of the acid, the ion $BiCl_4^-$ is probably formed and the ion $BiCl_5^{--}$ is formed at higher concentrations. They give,

$$BiOCl + 2H^+ + 3Cl^- = H_2O + BiCl_4^-, \quad K = 0.8.$$

From this value and the free energies of the other substances involved, the free energy of the complex chloride ion, $BiCl_4^-$, is −114,200 cal. The potential for the bismuth-complex chloride couple becomes,

$$4Cl^- + Bi = BiCl_4^- + 3e^-, \quad E^\circ = -0.16.$$

From the heat of formation, −90,600 cal., and the entropy of formation, −47.8 cal. per degree, the free energy of the solid trichloride, $BiCl_3(s)$ is −76,400 cal. One then finds for the solubility of the chloride in chloride ion,

$$BiCl_3(s) + Cl^- = BiCl_4^-, \qquad \Delta F^\circ = -6450 \text{ cal.}$$

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[58] Noyes, A. A., and Chow, M., J. Am. Chem. Soc., **40**, 739 (1918).

[59] Feitknecht, W., Helv. Chem. Acta, **16**, 1307 (1933).

[60] Noyes, A. A., Hall, F. W., and Beattie, J. A., J. Am. Chem. Soc., **39**, 2526 (1917).

Based on the free energy of the oxide obtained above, the free energy of solution in hydrochloric acid is,

$$Bi_2O_3(s) + H^+ + 8Cl^- = 2BiCl_4^- + 3H_2O, \qquad \Delta F^\circ = -31{,}100 \text{ cal.}$$

For the solubility product of bismuth sulfide, Kolthoff[61] reported,

$$Bi_2S_3 = 2Bi^{+++} + 3S^{--}, \qquad K = 1.6 \times 10^{-72}.$$

Bismuth monoxide. Bichowsky and Rossini give for the heat of formation of the monoxide, BiO, −49,500 cal. Using the value 17 cal. per degree for the entropy of the oxide, in analogy to lead monoxide, the entropy of formation is −21 and the free energy −43,200 cal. The potentials for the reduction and oxidation of the oxide are,

$$H_2O + Bi = BiO + 2H^+ + 2e^-, \qquad E^\circ = -0.29$$

$$BiO = BiO^+ + e^-, \qquad E^\circ = -0.38$$

For the decomposition of the oxide,

$$3BiO + 2H^+ = 2BiO^+ + Bi + H_2O, \qquad \Delta F^\circ = 3800 \text{ cal.}$$

These values may not be very accurate, but they do show that the oxide is stable in low acid and should decompose in high acid. These appear to be the experimental facts. Moreover the conditions for the formation of the oxide should be the reduction of +3 bismuth by a reducing agent, which is about the same strength as metallic bismuth, in a solution of low hydrogen ion. These conditions are met in the formation by reduction with Sn^{++}.

Bismuth tetroxide and pentoxide. Although it appears that the pentoxide, Bi_2O_5, and also its sodium salt can be prepared, they are very unstable and the commercial products are largely the tetroxide, Bi_2O_4, which is probably bismuthyl bismuthate $(BiO)BiO_3$. Baur and Lattmann[62] have studied the potential of the Bi_2O_3—Bi_2O_4 couple in alkaline solution. They found that Bi_4O_7 was an intermediate stage, and they reported for the potentials in 1 *M* NaOH,

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[61] Kolthoff, I. M., J. Phys. Chem., **35**, 2720 (1931).

[62] Baur, E., and Lattmann, W., Z. Elektrochem., **40**, 582 (1934).

$$2OH^- + 2Bi_2O_3 = Bi_4O_7 + H_2O + 2e^-, \qquad E^\circ = -0.51$$

$$2OH^- + Bi_4O_7 = 2Bi_2O_4 + H_2O + 2e^-, \qquad E^\circ = -0.62.$$

Correcting for the activity of the sodium hydroxide, we shall write,

$$2OH^- + Bi_2O_3 = Bi_2O_4 + H_2O + 2e^-, \qquad E^\circ_B = -0.56.$$

One then calculates for the free energy of the tetroxide, −109,000 cal., and for the couple in acid solution,

$$2H_2O + 2BiO^+ = Bi_2O_4 + 4H^+ + 2e^-, \qquad E^\circ = -1.59.$$

Since the ratio H^+/e^- is 2 for low acid and probably 4 for high acid, the potential in concentrated acid becomes much larger and the tetroxide will oxidize manganous to permanganate under these conditions.

The potential for the Bi_2O_3—pure Bi_2O_5 is probably about the same.

TABLE 21

GROUP V POTENTIALS IN ACID SOLUTION

−3		0		+3		+5
NH_4^+	−0.27	N_2	−1.44	HNO_2	−0.94	NO_3^-
PH_3	0.03	P	0.49	H_3PO_3	0.20	H_3PO_4
AsH_3	0.54	As	−0.247	$HAsO_2$	−0.56	H_3AsO_4
SbH_3	0.51	Sb	−0.212	SbO^+	−0.64	$Sb_2O_3^-$
BiH_3	ca 0.8	Bi	−0.32	BiO^+	ca −1.6	Bi_2O_5

Trends in the Group V potentials. In order to compare the various elements of Group V, the potentials for the more important oxidation-reduction couples in acid solution have been summarized in Table 21.

The XH_3 compounds increase in reducing power with increasing atomic weight. As mentioned above, the discrepancy in the arsenic and antimony values is doubtless an error in some of the thermal data. The oxygen compounds of the group are good or even powerful oxidizing agents with the exception of the compounds of phosphorus.

CHAPTER VIII

Carbon, Silicon, Germanium, Tin, and Lead

The elements of this group have four valence electrons and in the monatomic gas state these are s^2p^2. In their spectroscopic terms the elements are very much alike, but in the properties of their compounds there is but little similarity. The principal characteristic of the chemistry of carbon is its four tetrahedral electron pair bonds and the remarkable stability of these bonds with hydrogen, oxygen, nitrogen, sulfur, the halogens, and especially with other carbon atoms. The chemistry of silicon is very largely that of the dioxide and its many polyacids. With the heavier members of the family, the monoxide and dioxide become more basic, and the chemistry of the +2 and +4 ions assumes importance.

Carbon

The standard state of the element is β-graphite. Bichowsky and Rossini calculate from the data of Roth and Naeser[1] that the heats of transition of diamond to α- and β-graphite are −490 and −220 cal., respectively. Because of the difficulty of determining the type of graphite, these authors have taken diamond as their standard state. For the sake of conformity we shall use the β-graphite and add the constant figure 220 cal. per gram atom of carbon to their heats of formation.

Kelley[2] has reviewed the literature on the vapor pressure of carbon and records as the most probable values,

$$\text{C}(\beta\text{-graph.}) = \text{C(g)}, \qquad \Delta H^\circ = 199{,}050 \text{ cal. and } \Delta F^\circ = 187{,}430 \text{ cal.}$$

$$2\text{C}(\beta\text{-graph.}) = \text{C}_2\text{(g)}, \qquad \Delta H^\circ = 238{,}250 \text{ cal. and } \Delta F^\circ = 222{,}830 \text{ cal.}$$

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[1] Roth, W. A., and Naeser, W., Z. Elektrochem., **31**, 461 (1925).

[2] Kelley, K. K., U. S. Bur. Mines Bull., 383 (1935).

Oxidation states. To carbon in methane and its oxidation products, the following oxidation numbers may be assigned: CH_4, -4; CH_3OH, -2; HCHO, 0; HCOOH, $+2$; and CO_2, $+4$. This procedure conforms to our system of assigning oxidation numbers to other elements, and the only singular fact in this series is the failure of carbon in the zero state to separate as graphite instead of existing as the pseudohydrate, formaldehyde. If these were the only hydrogen and oxygen compounds of carbon, this anomaly would present no serious problem. Instead, however, we have thousands of compounds in which it is futile to attempt a classification of the carbon atoms in terms of the oxidation state. Of course, one may always write a half-reaction relating a given compound to the element, as, for example, for benzoic acid,

$$C_6H_5COOH = 7C + 2H^+ + 2H_2O + 2e^-.$$

But as such a half-reaction has no chemical significance, this classification of carbon in benzoic acid as having an average oxidation number of $-\frac{2}{7}$ is not useful. However there are many types of oxidation-reduction reactions in organic chemistry and fortunately it is not necessary to assign oxidation numbers in writing the corresponding half-reactions. A number of the more important cases will be considered.

The free energy of carbon compounds. The paucity of equilibrium data pertaining to carbon compounds has made the third law the most important and reliable source of free energies in this field. Parks and Huffman[3] in their excellent monograph have summarized the data on several hundred compounds. The values in Table 22 are taken from their work with the following exceptions:

The values of Kelley and Anderson[4] have been used for CO(g), CO_2(g) and H_2CO_3(aq). Bicarbonate and carbonate ions have been calculated from $K_1 = 4.31 \times 10^{-7}$ and $K_2 = 4.70 \times 10^{-11}$, which were chosen as the most probable values from the papers of MacInnes and his co-workers.[5] The data of Butler[6] have been used to calculate the free energy of solution of methyl alcohol. The free energy of solution of acetaldehyde is an estimate.

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[3] Parks, G. S., and Huffman, H. M., *Free Energies of Some Organic Compounds* (Chemical Catalog Co., New York, 1932).

[4] Kelley, K. K., and Anderson, C. T., U. S. Bur. Mines Bull., 384 (1935).

[5] MacInnes, D. A., and Belcher, D., J. Am. Chem. Soc., **55**, 2630 (1933); Shedlovsky, T., and MacInnes, D. A., J. Am. Chem. Soc., **57**, 1705 (1935).

[6] Butler, J. A. V., Trans. Faraday Soc., **33**, 229 (1937).

The free energy of formation of oxalate ion is obtained from the heat of formation, −195,160 cal., and the entropy of formation, −122.4 cal. per degree. The constants of the acid $K_1 = 5.9 \times 10^{-2}$ and $K_2 = 6.4 \times 10^{-5}$ are taken from the work of Gane and Ingold.[7] For the free energy of ionization of formic acid the value for the constant $K = 1.77 \times 10^{-4}$ is that given by Harned and Embree.[8]

TABLE 22

FREE ENERGIES OF IMPORTANT HYDROCARBONS AND THEIR OXIDATION PRODUCTS

(Values in calories at 25° C.)

Substance	ΔF°	Substance	ΔF°
$CO(g)$	−33,010	$HCOO^-$	−83,000
$CO_2(g)$	−94,450	$C_2H_5OH(l)$	−40,200
$H_2CO_3(aq)$	−149,170	$C_2H_5OH(aq)$	−41,850
HCO_3^-	−140,490	$CH_3CHO(l)$	−31,880
CO_3^{--}	−126,390	$CH_3CHO(aq)$	(−33,560)
$CH_4(g)$	−12,200	$CH_3COOH(l)$	−94,500
$C_2H_6(g)$	−10,700	$CH_3COOH(aq)$	−96,210
$C_2H_4(g)$	12,300	CH_3COO^-	−89,720
$C_2H_2(g)$	50,750	$H_2C_2O_4(aq)$	−166,060
$C_6H_5CH_3(l)$	26,800	$HC_2O_4^-$	−164,380
$CH_3OH(l)$	−39,960	$C_2O_4^{--}$	−158,660
$CH_3OH(aq)$	−42,110	$C_6H_5COOH(s)$	−60,100
$HCHO(aq)$	−31,020	$C_6H_5COOH(aq)$	−57,950
$HCOOH(l)$	−85,150	$C_6H_5COO^-$	−52,250
$HCOOH(aq)$	−88,110	$C_6H_{12}O_6(aq)$	−217,020

The oxidation of hydrocarbons. The potentials for the various steps in the oxidation of a hydrocarbon are of considerable interest, even though reversible equilibria cannot be attained at room temperature. The following half-reactions are calculated from the data in Table 22 for the oxidation of methane.

$$H_2O + CH_4(g) = CH_3OH(aq) + 2H^+ + 2e^-, \qquad E^\circ = -0.58$$

$$CH_3OH(aq) = HCHO(aq) + 2H^+ + 2e^-, \qquad E^\circ = -0.24$$

$$H_2O + HCHO(aq) = HCOOH(aq) + 2H^+ + 2e^-, \qquad E^\circ = 0.01$$

$$HCOOH(aq) = CO_2(g) + 2H^+ + 2e^-, \qquad E^\circ = 0.14$$

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[7] Gane, R., and Ingold, C. K., J. Chem. Soc., 2153 (1931).

[8] Harned, H. S., and Embree, N. D., J. Am. Chem. Soc., **56**, 1042 (1934).

It is rather surprising that methyl alcohol has such a high oxidizing potential. The reduction of carbon dioxide to formaldehyde, $E° = 0.08$, is of interest in connection with its absorption by plants. The schematic representation of these potentials in acid and akaline solutions is given below.

ACID

$$CH_4(g) \overset{-0.58}{\text{——}} CH_3OH(aq) \overset{-0.24}{\text{——}} HCHO(aq) \overset{0.01}{\text{——}} HCO_2H(aq) \overset{0.14}{\text{——}} CO_2(g)$$

ALKALINE

$$CH_4(g) \overset{0.25}{\text{——}} CH_3OH(aq) \overset{0.59}{\text{——}} HCHO(aq) \overset{1.14}{\text{——}} HCO_2^-(aq) \overset{0.95}{\text{——}} CO_3^{--}$$

For the oxidation of ethane, approximately the same values are obtained for corresponding steps, but here there is the added possibility of the oxidation of both carbon atoms.

$$H_2O + C_2H_6(g) = C_2H_5OH(aq) + 2H^+ + 2e^-, \quad E° = -0.55$$

$$C_2H_5OH(aq) = CH_3CHO(aq) + 2H^+ + 2e^-, \quad E° = -0.18$$

$$H_2O + CH_3CHO(aq) = CH_3COOH(aq) + 2H^+ + 2e^-, \quad E° = 0.13$$

$$2H_2O + CH_3COOH(aq) = H_2C_2O_4(aq) + 6H^+ + 6e^-, \quad E° = -0.31$$

$$H_2C_2O_4(aq) = 2CO_2(g) + 2H^+ + 2e^-, \quad E° = 0.49$$

From the last potential it should be relatively easy to oxidize oxalic acid to carbon dioxide, yet with as powerful an oxidizing agent as a permanganate the reaction is not rapid at room temperature.

Wurmser and DeBoe[9] measured the lactic acid–pyruvic acid couple,

$$CH_3CHOHCOOH = CH_3COCOOH + 2H^+ + 2e^-, \quad E° = -0.20$$

[9] Wurmser, R., and DeBoe, Z., Compt. rend., **194**, 2139 (1932).

A number of important free energy relations should also be noted. Formaldehyde is unstable with respect to the formation of glucose.

$$6HCHO(aq) = C_6H_{12}O_6(aq), \qquad \Delta F^\circ = -30{,}900 \text{ cal.}$$

This reaction appears to be a step in the synthesis of cellulose in plants.

Formaldehyde is also unstable with respect to its decomposition into carbon and water,

$$HCHO(aq) = C + H_2O, \qquad \Delta F^\circ = -25{,}670 \text{ cal.}$$

but there is no evidence that this reaction occurs.

From the potentials it is obvious that formaldehyde should oxidize and reduce itself, and experimentally the reaction goes slowly with the formation of methyl formate.

The equilibrium between carbon monoxide and formic acid has been studied by Branch.[10] From our free energy values we write,

$$HCOOH(aq) = CO(g) + H_2O, \qquad \Delta F^\circ = -1590 \text{ cal.}$$

For the oxidation of toluene to benzoic acid, one calculates from the free energies,

$$2H_2O + C_6H_5CH_3(l) = C_6H_5COOH(aq) + 6H^+ + 6e^-, \qquad E^\circ = -0.21.$$

This value is comparable with $E^\circ = -0.26$ for the CH_4-HCOOH half-reaction.

Electrolytic reduction of acids, aldehydes, and alcohols. A number of investigations have been made on the electrolytic reduction of carbonic acid or bicarbonate. Fischer and Prziza[11] report a 98 per cent reduction of carbon dioxide at 5 atm. pressure in potassium sulfate solution with an amalgamated zinc cathode, the reduction product being formic acid. These authors were unable to reduce carbon monoxide under similar conditions.

With high overvoltage cathodes, formic acid may be reduced to formaldehyde and methyl alcohol, and oxalic acid reduced to glyoxalic acid and glycollic acid. In certain cases, esters may be reduced electrolytically with the replacement of the –CO– group by $-CH_2-$ to form an ether.[12] In general, the reduction of monobasic aliphatic acids is difficult.

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[10] Branch, G. E. K., J. Am. Chem. Soc., **37**, 2316 (1915).

[11] Fischer, F., and Prziza, O., Ber., **47**, 256 (1914).

Müller[13] has reviewed the experimental facts and discussed the theory of the reduction of ketones, in particular for acetone, $(CH_3)_2CO$. The reduction products are: pinacol, $(CH_3)_2COH\text{-}COH(CH_3)_2$; isopropyl alcohol, $(CH_3)_2CHOH$; and propane, $CH_3CH_2CH_3$. The latter is produced with relatively high efficiency at amalgamated zinc and cadmium cathodes. This production of the propane is noteworthy in view of the fact that it is very difficult to reduce aldehydes or alcohols to the hydrocarbon. Müller has postulated a number of intermediates but little is actually known regarding the mechanism.

The cathodic reduction of an aldehyde forms the alcohol, and further reduction does not occur in spite of the favorable potential.

The anodic oxidation of certain aldehydes and alcohols in alkaline halide solutions results in the formation of the haloforms, for example,

$$C_2H_5OH + 3Cl^- + 7OH^- = CHCl_3 + CO_2 + 6H_2O + 10e^-$$

A number of cases are given by Swann.[14] However, the reaction mechanism is probably through the formation of the hypohalite.

The electrolytic oxidation of alcohols, aldehydes, and acids. In agreement with the potential values, it is easier to oxidize an aldehyde to the acid than it is to oxidize the alcohol to the aldehyde; consequently it is difficult in the anodic oxidation of a primary alcohol in acid solution to build up an appreciable concentration of the aldehyde, as the oxidation goes on to form the acid, except in special cases. In alkaline solution the anodic oxidation of primary alcohols results in the formation of hydrogen and hydrocarbons as well as the aldehyde. From these results, it appears that the intermediate formed is unstable with respect to its own oxidation and reduction. This instability also exists in the alcohols, for example, methyl alcohol should decompose into methane and formaldehyde but the reaction, of course, does not occur with appreciable speed. Müller and Hochstetter[15] have discussed the mechanism of the aldehyde oxidation.

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[12] Tafel, J., and Friedrichs, G., Ber., **37**, 3187 (1904).

[13] Müller, E., Z. Elektrochem., **33**, 253 (1927).

[14] Swann, S., Jr., Trans. Elektrochem. Soc., **69**, 296 (1936).

A somewhat similar result is obtained in the oxidation of aldehydes in alkaline solution. Thus, formaldehyde gives hydrogen and carbonate ion; and acetaldehyde yields formic acid, hydrocarbons, and some complex products. In acid solution, however, the aldehyde group is oxidized to carboxyl.

The anodic oxidation of acetic acid involves a number of points of unusual interest. The following experimental facts are significant:[16]

Two distinct reactions may occur. One, the Kolbe reaction, produces ethane and carbon dioxide,

$$2CH_3COOH \rightarrow C_2H_6 + 2CO_2 + 2H^+ + 2e^-, \qquad E^\circ = 0.16.$$

The other, the Hofer-Moest reaction, forms methyl alcohol and carbon dioxide,

$$H_2O + CH_3COOH \rightarrow CH_3OH + CO_2 + 2H^+ + 2e^-, \qquad E^\circ = -0.35.$$

The Kolbe reaction occurs with smooth platinum electrodes in concentrated acetate and acetic acid mixtures and the anodic potential is quite high, around −2.1 volts. The Hofer-Moest reaction is favored by the presence of high concentrations of alkali bicarbonates, sulfates, and other salts with negative ions which are not readily oxidized. It also occurs in acetic acid if salts of manganese, lead, or silver are present, as these substances appear to inhibit the Kolbe reaction. The anodic potential at which the Hofer-Moest reaction occurs is several tenths of a volt less than that for the Kolbe reaction.

Various theories of the oxidation mechanism are discussed in references cited. It seems probable that an intermediate is formed which may decompose to give the Hofer-Moest reaction, or if the conditions favor the stability of the intermediate, its concentration will build up until the rate of its reaction with acetic acid, to give the Kolbe reaction, becomes rapid. There is considerable uncertainty regarding the identity of the intermediate, but the strongest evidence points to a peroxyacetic acid, possibly CH_3CO_3H. On this assumption the following reactions may be written for an electrode of metal X, which has been oxidized to a surface layer of XOH.

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[15] Müller, E., and Hochstetter, F., Z. Elektrochem., **20**, 367 (1914).

[16] Cf. Glasstone, S., and Hickling, A., J. Chem. Soc., 1878 (1934); Fichter, F., Trans. Am. Electrochem. Soc., **56**, 467 (1929).

$$XOH + CH_3COO^- = CH_3CO_3H + X + e^-$$

$$CH_3CO_3H = CH_3OH + CO_2$$

$$CH_3CO_2H + CH_3CO_3H = C_2H_6 + 2CO_2 + H_2O$$

Higher fatty acids generally give the Kolbe reaction; and, in mixtures of two acids, hydrocarbons corresponding to R^1R^1, R^2R^2, and R^1R^2 are formed, as would be expected from the suggested mechanism.

Peroxycarbonate. The electrolysis of potassium carbonate solutions at low temperatures with a smooth platinum anode results in the formation of peroxycarbonate, $C_2O_6^{--}$. The di-acid appears to hydrolyze slowly to form the mono-acid, H_2CO_4. There are no experimental data regarding oxidizing power of the peroxycarbonates.

$$2H_2CO_3 = C_2O_6^{--} + 4H^+ + 2e^-, \qquad E^\circ < -1.7$$

Carbon as an oxidizing agent. Judging merely from the free energies, one would conclude that carbon was a fairly good oxidizing agent,

$$CH_4(g) = C + 4H^+ + 4e^-, \qquad E^\circ = -0.13$$

However in view of the high energy of the C–C bonds in solid, it is not surprising that the activation energy is so large that, even at a high overvoltage, carbon cannot be reduced to methane.

Carbon is thermodynamically stable with respect to its hydrolysis.

$$2C + 2H_2O = CO_2 + CH_4, \qquad \Delta F^\circ = 6730 \text{ cal.}$$

The positive free energy is not large; and, again, except for the high activation energy, appreciable partial pressures of the gaseous products would be obtained.

Unsaturated hydrocarbons. From the free energy data,

$$C_2H_6(g) = C_2H_4(g) + 2H^+ + 2e^-, \qquad E^\circ = -0.50$$

A similar case of the single bond-double bond couple is the succinic acid-fumaric acid electrode which was measured directly by Borsook and Schott.[17] They found,

$$\begin{aligned} &HO_2CCH_2 - CH_2CO_2H(aq) \\ &\quad = HO_2CH{=}CHCO_2H(aq) + 2H^+ + 2e^-, \qquad E^\circ = -0.44. \end{aligned}$$

It is again interesting to note that while the activation energy of these more complicated molecules is lower, the magnitude of the potential remains the same as for the C_2H_6—C_2H_4 couple.

The cathodic reduction of the double bonds of the benzene ring can be accomplished in the case of a number of its derivatives, for example, the reduction of phenol to cyclohexanol.[18]

For the double bond-triple bond potential, that is, the ethylene-acetylene couple, the computation from the free energies gives,

$$C_2H_4(g) = C_2H_2(g) + 2H^+ + 2e^-, \qquad E^\circ = -0.83$$

In spite of this favorable potential it is somewhat difficult to reduce acetylene. However, under suitable conditions it may be carried out electrolytically.

Aniline-nitrobenzene. Parks and Hoffman, in their monograph, gave for the free energy of aniline (l), 35,400 cal., and for nitrobenzene (l) a rough estimate of 36,400 cal. The solubility of aniline in water is about 0.3 *M* and the dissociation constant of the ion, $C_6H_5NH_3^+$, is 2×10^{-5}. As an approximate figure, 29,400 cal. will be taken for the free energy of the acid ion. Hence,

$$2H_2O + C_6H_5NH_3^+ = C_6H_5NO_2 + 7H^+ + 6e^-, \qquad E^\circ = -0.87$$

This potential is about the same as the value, -0.86, found for the NH_4^+—HNO_2 half-reaction. Haber and Schmidt[19] studied the electrolytic reduction of nitrobenzene and proposed a scheme which, with subsequent modification, is the following:

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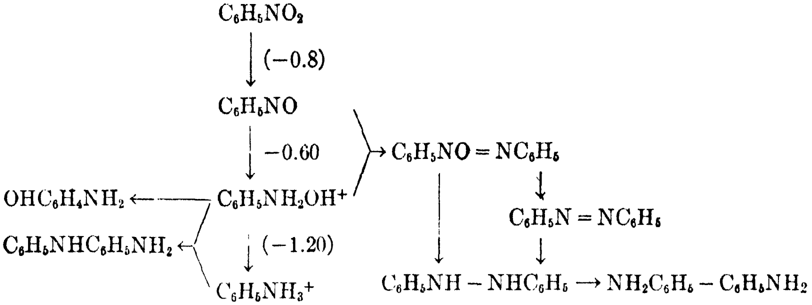
[17] Borsook, H., and Schott, H. F., J. Biol. Chem., **42**, 535 (1931).

[18] Cf. Bancroft, W. D., and George, A. B., Trans. Am. Electrochem. Soc., **57**, 399 (1930).

[19] Haber, F., and Schmidt, C., Z. physik. Chem., **32**, 271 (1900).



The first step, the formation of nitrosobenzene, requires a fairly high overvoltage. The second step, the formation of phenyl hydroxylamine, can attain a reversible equilibrium, and the potential of the couple has been measured.[20]

$$C_6H_5NH_2OH^+ = C_6H_5NO + 3H^+ + 2e^-, \qquad E^\circ = -0.60$$

The third step, the formation of aniline, is not reversible in the equilibrium sense. The potentials of the first and third steps have been estimated from the overall value and those of the corresponding simple nitrogen compounds. The formation of *p*-aminodiphenyl amine, $C_6H_5NHC_6H_5NH_2$; azoxybenzene, $C_6H_5NO:NC_6H_5$; and azobenzene, $C_6H_5N:NC_6H_5$ result from secondary reactions indicated by arrows. The azoxybenzene may be reduced to hydrazobenzene, $C_6H_5NH-NHC_6H_5$, which can rearrange to form benzidine. Also, rearrangement of the phenylhydroxylamine may occur to form *p*-aminophenol. Hydrazobenzene is not readily reduced to aniline, but a number of its substituted derivatives are. Reversible potentials have been measured for several of the substituted azobenzenes to the corresponding hydrazobenzenes and the E° values are about −0.4 (cf. International Critical Tables).

A cathode with high overvoltage favors the reduction of nitrobenzene to aniline in acid solution apparently because phenylhydroxylamine is then rapidly reduced and cannot therefore enter into side reactions. The side reaction producing azoxybenzene is favored by alkaline solutions.[21]

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[20] Cf. Conant, J. B., International Critical Tables, VI, 333.

A very complete review has been given by Swann[22] for the whole field of electrolytic organic oxidation and reduction reactions.

Cyanide, cyanate, and cyanogen. Data pertaining to these substances are summarized in Table 23. These values are recalculated from the data of Lewis and Randall, with the exception of $C_2N_2(g)$ which is calculated from the heat of formation, 70,560 cal., and the entropy of formation, 9.3 cal. per degree. The dissociation constant of hydrocyanic acid, 4×10^{-10}, by Harman and Worley[23] is probably better than the older values and has been employed in the recalculation. The third law free energy of HCN(g) appears to be 28,000 cal., which is in close agreement, but there is considerable uncertainty regarding the heat of formation. The following half-reactions relate the energies of the three oxidation states.

TABLE 23

FREE ENERGIES OF CYANOGEN DERIVATIVES

HCN(g)	27,730
HCN(aq)	26,340
CN^-	39,140
$C_2N_2(g)$	67,780
HCNO	−28,980
CNO^-	−23,630
K(HCN)	4×10^{-10}
K(HCNO)	1.2×10^{-4}

$$H_2O + \tfrac{1}{2}C_2N_2(g) = HCNO + H^+ + e^-, \quad E^\circ = 0.27$$

$$HCN = \tfrac{1}{2}C_2N_2(g) + H^+ + e^-, \quad E^\circ = -0.33$$

$$2OH^- + CN^- = CNO^- + H_2O + 2e^-, \quad E^\circ_B = 0.96$$

Cyanogen is unstable with respect to its so-called hydrolysis not only in alkaline solution but also in acid.

$$2OH^- + C_2N_2 = CN^- + CNO^- + H_2O, \quad \Delta F^\circ = -33{,}790 \text{ cal.}$$

$$H_2O + C_2N_2 = HCN + HCNO, \quad \Delta F^\circ = -13{,}730 \text{ cal.}$$

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[21] Glasstone, S., and Hickling, A., *Electrolytic Oxidation and Reduction* (Van Nostrand, New York, 1936), p. 161.

[22] Swann, S., Jr., Trans. Electrochem. Soc., **69**, 287 (1936).

[23] Harman, R. W., and Worley, F. P., Trans. Faraday Soc., **20**, 502 (1924).

Thiocyanate. From the thermal data of Bichowsky and Rossini,

$$CN^- + S = CNS^-, \qquad \Delta H^\circ = \Delta F^\circ = -16{,}000 \text{ cal.}$$

Since the entropy of the reaction must be small, the free energy may be taken equal to the ΔH°. This gives for the free energy of formation of thiocyanate ion, 23,140 cal. The heat of ionization of the acid is 330 cal.; and using the Pitzer[24] rule that the entropy of ionization is approximately 22 entropy units, the free energy of ionization is 5300 cal. and K = ca 1×10^{-4}. We shall then take 17,800 cal. as the free energy of HCNS. The most important potential is the oxidation to hydrogen cyanide and sulfurous acid.

$$3H_2O + HCNS \rightarrow HCN(aq) + H_2SO_3 + 4H^+ + 4e^-, E^\circ = -0.55$$

Bjerrum and Kirschner[25] found that free thiocyanogen was between bromine and iodine as an oxidizing agent and reported,

$$2CNS^- = (CNS)_2 + 2e^-, \qquad E^\circ = -0.77.$$

Hydroquinone-quinone couples. The reversibility of hydroquinone–quinone electrodes and their extensive use in the determination of hydrogen-ion concentrations are well known. Conant and Fieser[26] have given the potentials summarized in Table 24.

For those cases in which a solid quinhydrone is formed as an intermediate, the overall potential must obviously be measured in two steps. Thus for benzoquinone,

$$C_6H_4O_2 \cdot C_6H_4(OH)_2(s) = 2C_6H_4O_2(s) + 2H^+ + 2e^-, \qquad E^\circ = -0.749$$

$$2C_6H_4(OH)_2(s) = C_6H_4O_2 \cdot C_6H_4(OH)_2(s) + 2H^+ + 2e^-, \qquad E^\circ = -0.613.$$

Many additional quinone derivatives have been studied for the purpose of determining the effect of substitution upon the potential, but most of this work has been in nonaqueous solutions. Among the more important of these researches are: quinolinequinone and benzotriazole by Fieser and Martin,[27] naphthoquinones by Fieser and Fieser,[28] and various substituted quinones by Kvalnes.[29]

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[24] Pitzer, K. S., J. Am. Chem. Soc., **59**, 2365 (1937).

[25] Bjerrum, N., and Kirschner, A., Kgl. Danske Videnskab. Selskab. Math-fys., Series (8), Vol. **5**, No. 1, p. 76 (1918).

[26] Conant, J. B., and Fieser, L. F., J. Am. Chem. Soc., **45**, 2198 (1923); cf. also Schreiner, E., Z. physik. Chem., **117**, 64 (1925).

A very interesting review of the semiquinone problem has been given by Michaelis.[30]

TABLE 24

E° VALUES FOR SOME HYDROQUINONE-QUINONE COUPLES

Benzoquinone	−0.681	2-3 Dichloroquinone	−0.675
Toluquinone	−0.623	2-5 Dichloroquinone	−0.689
p-Xyloquinone	−0.582	2-6 Dichloroquinone	−0.698
Duroquinone	−0.480	Trichloroquinone	−0.670
Thymoquinone	−0.579	Tetrachloroquinone	−0.664
Monochloroquinone	−0.678		

Diphenylbenzidine and derivatives. Diphenylamine and its derivatives have become important as "inside" indicators for titrations with dichromate, ceric sulfate, and ferrous ion. Sarver and Kolthoff[31] have shown that diphenylamine is first oxidized irreversibly to diphenylbenzidine, and this is then oxidized reversibly to diphenylbenzidine violet. For this couple they gave,

$$C_6H_5NHC_6H_4 - C_6H_4NHC_6H_5 =$$

$$C_6H_5N{=}C_6H_4 - C_6H_4N{=}C_6H_5 + 2H^+ + 2e^-, \quad E^\circ = -0.76$$

For the more soluble sulfonic acid derivative these authors report $E^\circ = -0.87$. The higher potential of this couple is advantageous as it is desirable to have an indicator which is not oxidized by ferric ion. Hammett, Walden, and Edmonds[32] investigated *p*-nitrodiphenylamine and 2-4 diaminodiphenylamine and give, as E° values, −1.06 and −0.70, respectively.

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[27] Fieser, L. F., and Martin, E., J. Am. Chem. Soc., **57**, 1835 and 1840 (1935).

[28] Fieser, L. F., and Fieser, M., J. Am. Chem. Soc., **57**, 491 (1935).

[29] Kvalnes, D. E., J. Am. Chem. Soc., **56**, 670, 2487 (1934).

[30] Michaelis, L., Trans. Electrochem. Soc., **71**, 107 (1937).

[31] Sarver, L. A., and Kolthoff, I. M., J. Am. Chem. Soc., **53**, 2902 (1931).

[32] Hammett, L. P., Walden, G. H., and Edmonds, S. M., J. Am. Chem. Soc., **56**, 1092 (1934).

Indophenols. Clark and his co-workers[33] have measured the potentials of a number of leuco indophenol-indophenol couples. For the simplest type the reaction is

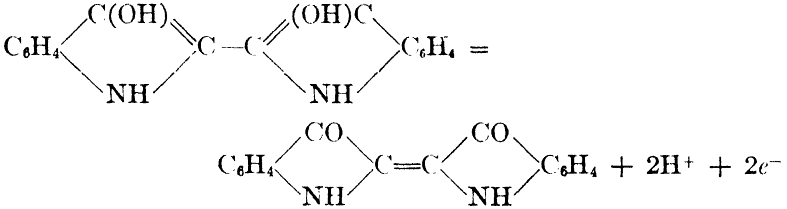
$$NH_2C_6H_4 - NH - C_6H_4OH = NH_2C_6H_4 - N{=}C_6H_4{=}O + 2H^+ + 2e^-.$$

The $E°$ values are complicated functions of the hydrogen-ion concentration and range from -0.55 to -0.7.

Methylene blue. The same authors have studied Lauth's violet and its tetramethyl derivative, methylene blue. The potentials are closely the same.

$$\text{Methylene white} = \text{methylene blue} + 2H^+ + 2e^-, \quad E° = -0.53$$

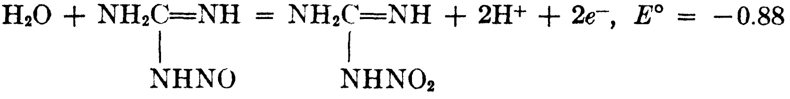
Indigo. The potentials for a number of leuco indigo-indigo couples have likewise been measured by Clark. The essential structural reaction is,



For a number of derivatives, the $E°$ values range from -0.26 to -0.37

Erioglaucine A. Knop[34] has studied the oxidation of erioglaucine A and eriogreen B. The oxidation potentials are -0.71 and -0.72, respectively. These dyes have been used as indicators in oxidation-reduction titrations but as the oxidized form is not very stable, the ferrous-phenanthroline complex (cf. p. 213) is to be preferred.

Nitroguanidine. Smith and Sabetta[35] report the following for nitroso-nitroguanidine:



$$H_2O + \underset{\displaystyle NHNO}{NH_2C{=}NH} = \underset{\displaystyle NHNO_2}{NH_2C{=}NH} + 2H^+ + 2e^-, \quad E° = -0.88$$

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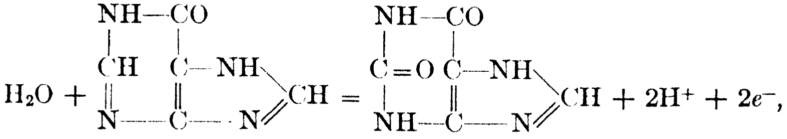
[33] Clark, W. M., *Determination of Hydrogen Ions* (Williams and Wilkins, Baltimore, 1928), p. 384. Cf. also International Critical Tables, **VI**, p. 333.

[34] Knop, J., Z. anal. Chem., **77**, 111 (1929).

[35] Smith, G. B. L., and Sabetta, V. J., J. Am. Chem. Soc., **54**, 1034 (1932).

Xanthines. Filitti[36] gave potentials for a number of xanthine couples,



$E^\circ = 0.01$

Flavines, murexides, and porphyrexide. Kuhn and his co-workers[37] have studied the oxidation and reduction of a large number of these complex nitrogen-carbon-oxygen ring structures. For the flavines, the E° values for pH = 7, range from −0.1 to −0.2; for porphyrexide, −0.72; and for murexides, −0.02.

Safranine. Stiehler, Chen, and Clark[38] investigated a number of safranine derivatives. The E° potentials are around −0.3.

Free energies of CS_2, COS, $COCl_2$, CCl_4, and $CO(NH_2)_2$. The Parks and Huffman monograph should be consulted for the free energies of many additional carbon compounds. The following values may frequently be found useful: $COCl_2(g)$, −48,960; $CCl_4(l)$, −15,600; COS(g), −39,800; $CS_2(l)$, 17,150; $CO(NH_2)_2(aq)$, −48,720.

The free energies of hydrolysis are readily calculable. Not many oxidation-reduction couples involving these substances are significant in aqueous solutions; however, urea is sometimes employed as a reducing agent, and this potential will be given. The constant for its basic dissociation is 1.5×10^{-14}, so we may write $CO(NH_2)_2$ even in acid solution.

$$H_2O + CO(NH_2)_2 \rightarrow CO_2 + N_2 + 6H^+ + 6e^-, \qquad E^\circ = -0.1$$

Silicon

The standard state of the element is the crystalline solid. Ruff and Konschak[39] from their vapor pressure measurements estimated 85,000 cal. as the heat of sublimation, but Wartenberg[40] calculated from his data only 44,000 cal. The entropy of sublimation is 35.6 cal. per degree.

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[36] Filitti, S., J. chim. phys., **32**, 1 (1935).

[37] Kuhn, R., Ber., **68**, 1528 (1935); *ibid.*, **69**, 1547 and 1557 (1936).

[38] Stiehler, R., Chen, T., and Clark, W. M., J. Am. Chem. Soc., **55**, 891 (1933).

[39] Ruff, O., and Konschak, M., Z. Elektrochem., **32**, 515 (1926).

[40] Wartenberg, H. v., Z. Elektrochem., **19**, 482 (1913).

Oxidation states. The principal oxidation state, +4, is that of the dioxide, SiO_2, and the tetrahalides. The dioxide forms innumerable acids, the ortho- forms of the mono-, di-, tri-, and tetra-acids being H_4SiO_4, $H_6Si_2O_7$, $H_8Si_3O_{10}$, and $H_{10}Si_4O_{13}$, respectively; and many dehydrated forms of these acids are also known, for example, meta-mono-silicic acid, H_2SiO_3. In aqueous solutions these acids are often present in complicated equilibria; hence it appears that the difference in free energy between the various poly-acids is small. Silicous acid, $H_2Si_2O_3$, is formed by the hydrolysis of the hydrogen halides, $SiHX_3$, and this acid may be classified as belonging to the +2 oxidation state. The existence of the monoxide is doubtful. A number of hydrosilicons and their derivatives, analogous to the corresponding carbon compounds, are known, but they are relatively unstable and their free energies, with the exception of SiH_4, cannot be calculated at present.

TABLE 25

ENTROPIES, HEATS, AND FREE ENERGIES OF FORMATION OF SILICON COMPOUNDS

Substance	S (Compounds)	$\Delta S°$	$\Delta H°$	$\Delta F°$
$SiO_2(\alpha$ quartz$)$	10.1	−43.4	−203,340	−190,400
$H_2SiO_3(s)$	(21)	−88	−274,100	−247,900
$SiF_4(g)$	(70)	−30.5	−360,100	−351,000
SiF_6^{--}	(40)	−140	−544,000	−502,500
$SiCl_4(l)$	57.4	−53.7	−150,100	−134,100
$SiH_4(g)$	49.03	−18	−8,700	−3,300
$SiC(s)$	3.9	−2.0	−27,800	−27,200

The free energies of some silicon compounds. The calculations from thermal data leading to the free energies of a few silicon compounds are summarized in Table 25.

The heats of formation are from Bichowsky and Rossini, except that for H_2SiO_3. Their value for this substance was based largely upon the heat of hydration of silicon dioxide calculated by Thiessen and Koerner[41] from their vapor pressure data. Their value leads to an improbable entropy of hydration, so their vapor pressure data were used and the heat consistent with the entropy was estimated. The $\Delta H°$ for silane is from the equilibrium data by Wartenberg.[42] However, the later investigation by Hogness,

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[41] Thiessen, P. A., and Koerner, O., Z. anorg. allgem. Chem., **197,** 307 (1931).

[42] Wartenberg, H. v., *Nernsts Festschrift* (Knapp, Halle, 1912), p. 459.

Wilson, and Johnson[43] casts some doubt upon the validity of this work.

Oxidation and reduction of silicon. Like the case of carbon, the bonds between the atoms in the solid silicon are so strong that the activation energies in reactions involving the free element are very large. Consequently the oxidation-reduction couples of silicon are not thermodynamically reversible at low temperatures. However the energy relations in the following cases are of some interest.

$$SiH_4(g) = Si + 4H^+ + 4e^-, \qquad E^\circ = -0.04$$

$$4OH^- + SiH_4(g) = Si + 4H_2O + 4e^-, \qquad E^\circ_B = 0.79$$

$$2H_2O + Si = SiO_2 + 4H^+ + 4e^-, \qquad E^\circ = 0.84$$

$$3H_2O + Si = H_2SiO_3 + 4H^+ + 4e^-, \qquad E^\circ = 0.84$$

$$6F^- + Si = SiF_6^{--} + 4e^-, \qquad E^\circ = 1.17$$

Only a very approximate value can be given for the free energies of the silicate ions in alkaline solution. Mulert[44] has given values for the heats of solutions of various hydrates of silicon dioxide but his data do not appear to be consistent with reasonable estimations of the free energies and entropies of solution. Several determinations of the ionization constants of the simpler silicic acids have been made. For H_2SiO_3, Joseph and Oakley[45] reported $K_1 = 10^{-10}$ and $K_2 = 10^{-12}$. Considering these values and rough figures for the solubility of the acid, the free energy of SiO_3^{--} is estimated as ca −215,000 cal.

$$6OH^- + Si = SiO_3^{--} + 3H_2O + 4e^-, \qquad E^\circ_B = 1.73$$

From this figure, the free energy is very favorable for the solution of silicon in alkali with the evolution of hydrogen.

Silicon is also thermodynamically unstable with respect to its hydrolysis reaction,

$$2Si + 2H_2O = SiH_4(g) + SiO_2, \qquad \Delta F^\circ = -80{,}300 \text{ cal.}$$

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[43] Hogness, T. R., Wilson, T. L., and Johnson, W. C., J. Am. Chem. Soc., **58**, 108 (1936).

[44] Mulert, O., Z. anorg. Chem., **75**, 198 (1912).

[45] Joseph, A. F., and Oakley, H. B., J. Chem. Soc., **127**, 2813 (1925).

Equilibria involving the silicon halides. Kubelka and Pristoupil[46] have investigated the reaction of the dioxide with hydrogen fluoride. They record,

$$SiF_6^{--} + 2H_2O = SiO_2 + 4H^+ + 6F^-, \qquad K = 2 \times 10^{-27},$$
$$\Delta F^\circ = 36{,}500 \text{ cal.}$$

From our free energies we calculate 31,300 cal. for this reaction. Considering the very large free energies of the substances involved and the approximate nature of much of the data, the agreement is about all that could be expected.

For the equilibrium between the fluosilicate and the tetrafluoride we calculate,

$$SiF_6^{--} = SiF_4(g) + 2F^-, \qquad \Delta F^\circ = 20{,}100 \text{ cal.}$$

and for the partial hydrolysis which occurs when the tetrafluoride is passed into water,

$$3SiF_4(g) + 3H_2O = 2H_2SiF_6(aq) + H_2SiO_3(s),$$
$$\Delta F^\circ = -24{,}820 \text{ cal.}$$

For the hydrolysis of the tetrachloride our free energies give,

$$SiCl_4(l) + 2H_2O = SiO_2 + 4H^+ + 4Cl^-, \ \Delta F^\circ = -68{,}300 \text{ cal.}$$

Germanium

The standard state of the element is the crystalline solid. There are no data on the vapor pressure or heat of vaporization.

Oxidation states. Germanium forms oxides of the +2 and +4 oxidation states, GeO and GeO_2. Both oxides are amphoteric. Evidence has been advanced indicating that germanous acid has a formic acid structure or at least may exist in this tautomeric form, but with hydrochloric acid it forms $GeCl_2$ and with hydrogen sulfide, GeS. The evidence does not appear to be conclusive. Germane, GeH_4, and a number of hydrogen compounds analogous to the simple hydrocarbons, are known, but no thermodynamic data have been obtained for them.

Germanium potentials. Nichols and Cooper[47] sought to measure the Ge—GeO_2 couple but concluded that the cell was not completely reversible. The heat of formation of the dioxide has not been determined. Laubengayer and Morton[48] studied the crystal forms of the dioxide. The tetragonal rutile type of the oxide is practically insoluble and much denser than the soluble hexagonal form, and the difference in energy between the two appears to be unusually large. No hydrates of the more soluble modification are known. Its solubility is given as 4.55 g per liter at 25° C. From the data on neighboring elements, an estimate of $-155{,}000$ cal. is made for the heat of formation of the soluble modification and $-142{,}000$ cal. for its free energy,

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[46] Kubelka, P., and Pristoupil, V., Z. anorg. allgem. Chem., **197,** 391 (1931).

[47] Nichols, M. L., and Cooper, S. R., Ind. Eng. Chem., Anal. Ed., **7,** 350 (1935).

$$2H_2O + Ge = GeO_2 + 4H^+ + 4e^-, \qquad E^\circ = \text{ca } 0.3$$

Pugh[49] has given the constants of the acid H_2GeO_3 as K_1, 2.6×10^{-9} and K_2, 1.9×10^{-13}. Combining with the solubility we find,

$$GeO_2 + H_2O = H^+ + HGeO_2^-, \qquad K = 1.1 \times 10^{-10}$$

For the potential in alkaline solution we may then write,

$$5OH^- + Ge = HGeO_3^- + 2H_2O + 4e^-,$$

$$E_B^\circ = \text{ca } 1.2.$$

Roth and Schwartz[50] measured the heat of hydrolysis of $GeCl_4(l)$ and recorded 25 kcal. Estimating the entropy of the reaction as 27 cal. per degree, we find,

$$2H_2O + GeCl_4(l) = GeO_2 + 4H^+ + 4Cl^-,$$

$$\Delta F^\circ = -17{,}000 \text{ cal.}$$

In hot concentrated hydrochloric acid the reaction is reversed and the dioxide may be converted to the volatile tetrachloride. The complex fluoride ion, GeF_6^{--}, forms, but there are no quantitative data.

Acid solutions of Ge^{++} are fairly stable in the absence of oxidizing agents but highly alkaline solutions evolve hydrogen with the oxidation of the germanium to $HGeO_3^-$. At the same time some decomposition into the metal and the germanate is said to occur. With reference to the Ge—GeO_2 couples, we estimate,

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[48] Laubengayer, A. W., and Morton, D. S., J. Am. Chem. Soc., **54,** 2318 (1932).

[49] Pugh, W., J. Chem. Soc., 2001 (1929).

[50] Roth, W. A., and Schwartz, O.; Z. physik. Chem., **134,** 456 (1928).

$$2H_2O + Ge^{++} = GeO_2 + 4H^+ + 2e^-, \qquad E^\circ = \text{ca } 0.2$$

$$2OH^- + HGeO_2^- = HGeO_3^- + H_2O + 2e^-, \qquad E_B^\circ = \text{ca } 1.4$$

Both the +2 and +4 sulfides may be precipitated. The latter is readily soluble in sulfide ion with the formation of thiogermanate. No values for the equilibrium constants can be given.

The cathodic reduction of a germanium electrode in phosphoric acid results in the formation of some GeH_4. The compound appears to be endothermic, but a fairly high temperature is required for its decomposition.

$$GeH_4 = Ge + 4H^+ + 4e^-, \qquad E^\circ > 0.3$$

There are few elements whose chemistry is so little understood as is that of germanium. The almost complete lack of quantitative data is to be noted, and many of the qualitative facts upon which the approximate potentials have been estimated will doubtless be subject to reinterpretation.

Tin

The standard state of the element is the metal. Two metallic forms are known, rhombic and tetragonal; but, as the difference in energy is only 2 cal., either may be taken as the standard state. Lewis and Randall[51] gave $\Delta H^\circ = 532$, $\Delta S^\circ = 1.94$, and $\Delta F^\circ = 9.5$ for the transition of the nonmetallic gray modification to the metallic. Kelley[52] calculates 61,940 cal. as the free energy of vaporization to form Sn_4(g) from the vapor pressure measurements of Harteck, but concluded that the results of a number of investigators who worked at higher temperatures than Harteck could not be reconciled with assumption of the tetratomic gas.

Oxidation states. Tin exists in the +2 oxidation state, stannous and stannite compounds, and in the +4 state, stannic and stannate compounds. The hydrogen compound, SnH_4, may be prepared but it is thermodynamically unstable.

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[51] Lewis, G. N., and Randall, M., *Thermodynamics* (McGraw-Hill, New York, 1923), p. 450.

[52] Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).

Tin-stannous potentials. The International Critical Tables chose for the Sn—Sn^{++} couple,

$$Sn = Sn^{++} + 2e^-, \qquad E^\circ = 0.136$$

and the free energy of Sn^{++}, -6275 cal.

Derived from the heat of formation of stannous hydroxide, $-136{,}100$ cal., and the entropy of formation, -70 cal. per degree, which is based upon an estimate of 22 for the entropy of $Sn(OH)_2$, the free energy of formation is $-115{,}200$ cal. This gives for the solubility product, 1.6×10^{-25}. Experimental values in the literature are 5×10^{-25} by Prytz[53] and 1.4×10^{-28} by Smrz.[54] We are unable to locate the cause of the discrepancy and shall adopt the value of Prytz.

$$Sn(OH)_2 = Sn^{++} + 2OH^-, \qquad K = 5 \times 10^{-26}.$$

The corresponding free energy of the hydroxide is $-115{,}950$ cal. Smrz also reported for the acid dissociation,

$$H_2SnO_2 = H^+ + HSnO_2^-, \qquad K = 6 \times 10^{-18}.$$

From this value the free energy of formation of the ion, $HSnO_2^-$, is $-92{,}450$ cal., and

$$3OH^- + Sn = HSnO_2^- + H_2O + 2e^-, \qquad E_B^\circ = 0.79.$$

However, stannite is unstable with respect to its decomposition into tin and stannate (cf. stannate).

We may also calculate the free energy of stannous sulfide from its heat of formation, $-22{,}700$ cal. Assuming the entropy of the sulfide to be 15, the entropy of formation is 4.9 and the free energy is $-21{,}250$ cal.

$$SnS = Sn^{++} + S^{--}, \qquad K = 8 \times 10^{-29}$$

$$S^{--} + Sn = SnS + 2e^-, \qquad E^\circ = 0.97$$

Stannous carbonate is hydrolyzed to the hydroxide.

Stannous-stannic potentials. An accurate value for the Sn^{++}—Sn^{+4} couple cannot be given, as the activity coefficient and hydrolysis constant of stannic ion are not known. Huey and Tartar[55] reported -0.154 and we shall write,

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[53] Prytz, M., Z. anorg. allgem. Chem., **174**, 371 (1928).

[54] Smrz, J., Rec. trav. chim., **44**, 590 (1925).

$$Sn^{++} = Sn^{+4} + 2e^-, \qquad E^\circ = -0.15$$

The corresponding free energy of stannic ion is ca 650 cal. Prytz[56] attempted to measure the Sn—Sn^{+4} couple in perchlorate solution but we are unable to interpret his results.

The thermal data on stannic hydroxide (precipitated) do not appear to be very reliable, but we shall use the Bichowsky and Rossini value, $-269{,}000$ cal. An estimate of 29 for the entropy of the hydroxide is probably fairly close. This then gives -144 for the entropy of formation and $-226{,}000$ cal. for the free energy.

$$Sn(OH)_4 = Sn^{+4} + 4OH^-, \quad K = \text{ca } 10^{-56}$$

From the rather sketchy data on the hydrolysis of stannate ion, $Sn(OH)_6^{--}$, we estimate,

$$Sn(OH)_4 + 2OH^- = Sn(OH)_6^{--}, \quad \Delta F^\circ = -5000 \text{ cal.}$$

An approximate value for the free energy of stannate is then $-306{,}000$ cal.

$$H_2O + 3OH^- + HSnO_2^- = Sn(OH)_6^{--} + 2e^-,$$

$$E^\circ_B = 0.96$$

From the free energies of stannite and stannate one computes,

$$2H_2O + 2HSnO_2^- = Sn + Sn(OH)_6^{--},$$

$$\Delta F^\circ = -7700 \text{ cal.}$$

This energy appears very reasonable in view of the experimental decomposition of stannite solutions and is a gratifying check upon the validity of our free energies. No data can be given for the insoluble β stannic acid.

From the thermal data, we estimate for the free energy of the complex fluoride, SnF_6^{--}, $-436{,}000$ cal. However this figure makes tin in the presence of fluoride ion so highly electropositive that one is inclined to question the thermal data.

The heat of formation of $SnCl_4(l)$ is given as $-127{,}400$ cal.

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[55] Huey, C. S., and Tartar, H. V., J. Am. Chem. Soc., **56**, 2585 (1934).

[56] Prytz, M., Z. anorg. allgem. Chem., **219**, 89 (1934).

The entropy of formation is −56.8 cal. per degree, and these values then give −110,600 cal. for the free energy. For the free energy of hydrolysis, one computes,

$$SnCl_4(l) + 4H_2O = Sn(OH)_4 + 4H^+ + 4Cl^-, \qquad \Delta F^\circ = -14,000 \text{ cal.}$$

Since the hydroxide is quite soluble in hydrochloric acid, the actual chemical reaction forms considerable stannic ion in solution. The complex ion, $SnCl_6^{--}$, doubtless is present at high chloride concentrations but no value can be given for its free energy.

No quantitative work has been done on stannic sulfide or the thiostannates. From the fact that stannous sulfide is oxidized by polysulfide, we may write,

$$2S^{--} + SnS = SnS_3^{--} + 2e^-, \qquad E^\circ > 0.6$$

Lead

The standard state of the element is the solid metal. From the Bichowsky and Rossini ΔH° of sublimation, 47,500 cal. and the ΔS°, 26.4 cal. per degree, the free energy of sublimation is 39,600 cal. The saturated lead amalgam is frequently used as an electrode and a number of investigators have found

$$Pb(s) = Pb(\text{sat. amal.}), \qquad \Delta F^\circ = -270 \text{ cal.}$$

Oxidation states. The plumbous ion, Pb^{++}, is stable in acid solution and forms salts with most negative ions; the hydroxide is amphoteric and plumbite ion is formed in alkaline solutions. The +4 oxide, PbO_2, is also amphoteric but is rather inert toward both H^+ and OH^-. The oxide, Pb_3O_4, is a plumbous orthoplumbate, Pb_2PbO_4; and Pb_2O_3 is probably $PbPbO_3$. Many investigators have claimed the existence of the +1 oxide, Pb_2O, but Van Arkel[57] has shown by X-ray analysis that it is a mixture of the tetragonal (red) PbO and the metal.

Lead-plumbous and lead-plumbite couples. Randall and

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[57] Van Arkel, A. E., Rec. trav. chim., **44**, 652 (1925).

Cann[58] reported 0.1213 for the Pb—Pb^{++} couple. Carmody[59] found 0.1263 and Fromherz[60] gave 0.1274. We shall write,

$$\mathrm{Pb} = \mathrm{Pb}^{++} + 2e^-, \qquad E^\circ = 0.126$$

The corresponding free energy of lead ion is −5810 cal.

Spencer and Mote[61] gave the following free energies: PbO (red), −45,100 cal.; PbO (yellow), −44,956 cal.; and $\mathrm{PbO}\cdot\frac{1}{3}\mathrm{H_2O}$, −63,721 cal. Combining these with the free energy of solution of PbO in hydroxide obtained by Randall and Spencer,[62]

$$\mathrm{PbO(r)} + \mathrm{OH}^- = \mathrm{HPbO_2}^-, \qquad \Delta F^\circ = 1903 \text{ cal.}, \quad K = 4.03 \times 10^{-2}$$

$$\mathrm{PbO(y)} + \mathrm{OH}^- = \mathrm{HPbO_2}^-, \qquad \Delta F^\circ = 1740 \text{ cal.}, \quad K = 5.31 \times 10^{-2}$$

The free energy of the biplumbite ion is −80,800 cal.

$$3\mathrm{OH}^- + \mathrm{Pb} = \mathrm{HPbO_2}^- + \mathrm{H_2O} + 2e^-, \qquad E_B^\circ = 0.54$$

$$2\mathrm{OH}^- + \mathrm{Pb} = \mathrm{PbO(r)} + \mathrm{H_2O} + 2e^- \qquad E_B^\circ = 0.578$$

Using for the heat of formation of $\mathrm{Pb(OH)_2}$(ppt.), −123,000 cal., and estimating the entropy of the hydroxide as 23, we calculate from the third law, $\Delta F^\circ = -102{,}200$ cal.

$$\mathrm{Pb(OH)_2} = \mathrm{Pb}^{++} + 2\mathrm{OH}^-, \qquad K = 2.8 \times 10^{-16}$$

Randall and Spencer gave for this constant, 8.7×10^{-16}.

From our free energies,

$$\mathrm{Pb(OH)_2} = \mathrm{H}^+ + \mathrm{HPbO_2}^-, \qquad K = 2.1 \times 10^{-16}$$

The value given by Smrz[63] is 1.5×10^{-15}. However there is considerable doubt regarding the composition of the solid phase, and although $\mathrm{Pb(OH)_2}$ may first be formed upon precipitation, the solid at equilibrium may be $\mathrm{Pb(HPbO_2)_2}$ or other complex hydrates, or even a solid solution of two or more hydrates. For the solubility product it is probably better to write,

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[58] Randall, M., and Cann, J. Y., J. Am. Chem. Soc., **52**, 589 (1930). Cf. Cann, J. Y., and La Rue, E., J. Am. Chem. Soc., **54**, 3456 (1932).

[59] Carmody, W. R., J. Am. Chem. Soc., **51**, 2905 (1929); **54**, 210 (1932).

[60] Fromherz, H., Z. physik. Chem., **153**, 387 (1931).

[61] Spencer, H. M., and Mote, J. H., J. Am. Chem. Soc., **54**, 4618 (1932).

[62] Randall, M., and Spencer, H. M., J. Am. Chem. Soc., **50**, 1572 (1928).

[63] Smrz, J., Rec. trav. chim., **44**, 590 (1925).

$$PbO(r) + H_2O = Pb^{++} + 2OH^-, \qquad K = 5.5 \times 10^{-16}$$

Plumbous halides. The potentials of cells having the reaction,

$$Pb + 2AgX = PbX_2 + 2Ag$$

where X is Cl, Br, or I, have been measured by a number of investigators. Thus for chloride and iodide, Gerke[64] reported the E° values 0.490 and 0.2135; and for bromide, Cann and Sumner[65] gave 0.3525. Cann and Taylor[66] agree closely with Gerke's value for the iodide. Combining with our values for the Ag—AgX couples we find:

$$2Cl^- + Pb = PbCl_2 + 2e^-, \qquad E^\circ = 0.268$$

$$2Br^- + Pb = PbBr_2 + 2e^-, \qquad E^\circ = 0.280$$

$$2I^- + Pb = PbI_2 + 2e^-, \qquad E^\circ = 0.365.$$

The corresponding free energies are $PbCl_2$, −75,040 cal.; $PbBr_2$, −62,060 cal.; and PbI_2, −41,470 cal.; and the solubility products, are:

$$PbCl_2 = Pb^{++} + 2Cl^-, \qquad K = 1.7 \times 10^{-5}$$

$$PbBr_2 = Pb^{++} + 2Br^-, \qquad K = 6.3 \times 10^{-6}$$

$$PbI_2 = Pb^{++} + 2I^-, \qquad K = 8.7 \times 10^{-9}$$

Fromherz,[67] in his careful work on the lead halide activities, has shown the existence of relatively high concentrations of PbX^+ ions. He gave the following constants:

$$PbCl^+ = Pb^{++} + Cl^-, \qquad K = 0.0775$$

$$PbBr^+ = Pb^{++} + Br^-, \qquad K = 0.071$$

$$PbI^- = Pb^{++} + I^-, \qquad K = 0.0345$$

Concentrated solutions of halide ions dissolve the lead halides with the formation of the complex ions, but no quantitative data can be given.

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[64] Gerke, R. H., J. Am. Chem. Soc., **44**, 1684 (1922).
[65] Cann, J. Y., and Sumner, R. A., J. Phys. Chem., **36**, 2615 (1932).
[66] Cann, J. Y., and Taylor, A. C., J. Am. Chem. Soc., **59**, 1989 (1937).
[67] Fromherz, H., Z. physik. Chem., **153**, 382 (1931).

Kohlrausch[68] recorded

$$PbF_2 = Pb^{++} + 2F^-, \qquad K = 3.7 \times 10^{-}_{8}$$

The constant is probably not very accurate, but a rough value calculated from the thermal data is of the same order of magnitude.

Additional lead-plumbous couples. From the $\Delta H°$ of formation of lead sulfide, −22,300 cal., and the $\Delta S°$, −1.3, which is accurately known, $\Delta F°$ is −21,910 cal.

$$PbS = Pb^{++} + S^{--}, \qquad K = 1.0 \times 10^{-29}$$

Kolthoff[69] gave 3.4×10^{-28} for the constant from equilibria data but the third law value is probably as reliable although there is some uncertainty in the $\Delta H°$.

$$S^{--} + Pb = PbS + 2e^-, \qquad E° = 0.98$$

The Pb—PbSO₄ couple is an important reference electrode and also one of the electrodes in the lead storage battery. Harned and Hamer,[70] in their critical survey of the subject, record,

$$SO_4^{--} + Pb = PbSO_4 + 2e^-, \qquad E° = 0.355$$

their general equation for the temperature range of 0° to 60° C. being,

$$E° = 0.33096 + 9.5244 \times 10^{-4}t + 8.069 \times 10^{-7}t^2.$$

We shall use this value, although Shrawder and Cowperthwaite,[71] extrapolating to the limiting Debye-Hückel slope, found $E° = 0.35052$ for the Pb(sat. amal.)—$PbSO_4$ couple, which would give, for the $E°$ against the metal, 0.3563.

Combining with our free energies this gives,

$$PbSO_4, \ \Delta F° \text{ (formation)} = -159{,}500 \text{ cal.}$$

$$PbSO_4 = Pb^{++} + SO_4^{--}, \qquad K = 1.8 \times 10^{-8}$$

Jowett and Price[72] gave the following constants for the lead phosphates,

$$Pb_3(PO_4)_2 = 3Pb^{++} + 2PO_4^{---}, \qquad K = 3 \times 10^{-44}$$

$$PbHPO_4 = Pb^{++} + HPO_4^{--}, \qquad K = 4 \times 10^{-12}.$$

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[68] Kohlrausch, F., Z. physik. Chem., **64**, 146 (1908).

[69] Kolthoff, I. M., J. Phys. Chem., **35**, 2720 (1931).

[70] Harned, H. S., and Hamer, W. J., J. Am. Chem. Soc., **57**, 33 (1935).

[71] Shrawder, J., Jr., and Cowperthwaite, I. A., J. Am. Chem. Soc., **56**, 2343 (1934).

[72] Jowett, M., and Price, H. I., Trans. Faraday Soc., **28**, 668 (1932).

For lead iodate, Geilmann and Höltje[73] reported,

$$Pb(IO_3)_2 = Pb^{++} + 2IO_3^-, \qquad K = 3.2 \times 10^{-13}.$$

MacDougall and Hoffman[74] gave for the solubility product of lead bromate,

$$Pb(BrO_3)_2 = Pb^{++} + 2BrO_3^-, \qquad K = 2.0 \times 10^{-2}.$$

Beck[75] studied the solubility product of lead chromate.

$$PbCrO_4 = Pb^{++} + CrO_4^{--}, \qquad K = 1.8 \times 10^{-14}$$

Kelley[76] has reviewed the data on lead carbonate and calculates the following free energies of formation: $PbCO_3$, $-149{,}710$ cal., and $PbO \cdot PbCO_3$, $-195{,}240$ cal. Combining with our free energies for the ions, we compute,

$$PbCO_3 = Pb^{++} + CO_3^{--}, \qquad K = 1.5 \times 10^{-13}$$

$$CO_3^{--} + Pb = PbCO_3 + 2e^-, \qquad E^\circ = 0.506.$$

Randall and Spencer[77] found for basic lead carbonate,

$$Pb_3(CO_3)_2(OH)_2 + 7OH^- = 3HPbO_2^- + 2CO_3^{--} + 3H_2O, \qquad \Delta F^\circ = 6961 \text{ cal.}$$

This would give, for the free energy of the basic carbonate, $-409{,}115$ cal., and

$$2OH^- + 2CO_3^{--} + 3Pb = Pb_3(CO_3)_2(OH)_2 + 6e^-, \qquad E^\circ_B = 0.59$$

Plumbous-plumbic couples. The most critical investigation of any plumbous-plumbic couple appears to be the work of Harned and Hamer[78] on the $PbSO_4$—PbO_2 couple. These authors found,

$$2H_2O + PbSO_4 = PbO_2 + SO_4^{--} + 4H^+ + 2e^-, \qquad E^\circ = -1.685.$$

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[73] Geilmann, W., and Höltje, R., Z. anorg. allgem. Chem., **152**, 65 (1926).

[74] MacDougall, F. H., and Hoffman, E. J., J. Phys. Chem., **40**, 330 (1936).

[75] Beck, K., Z. Elektrochem., **17**, 846 (1911).

[76] Kelley, K. K. and Anderson, C. T., U. S. Bur. Mines Bull. 384 (1935).

[77] Randall, M., and Spencer, H. M., J. Am. Chem. Soc., **50**, 1582 (1928).

[78] Harned, H. S., and Hamer, W. J., J. Am. Chem. Soc., **57**, 33 (1935).

This value, with those of the Pb—$PbSO_4$ and Pb—Pb^{++} couples, then gives,

$$2H_2O + Pb^{++} = PbO_2 + 4H^+ + 2e^-, \qquad E^\circ = -1.456$$

One then computes the free energy of formation of PbO_2 to be −52,020 cal. From the work of Glasstone,[79]

$$PbO_2 + H_2 = PbO + H_2O, \qquad \Delta F^\circ = -49{,}600$$

and this would make the free energy of the PbO_2, −52,190 cal. Based on the Bichowsky and Rossini ΔH°, −65,000 cal. and the ΔS°, 46.2 cal. per degree, the ΔF° is −51,210 cal. Andrews and Brown,[80] from cell measurements, report −50,600 cal. We shall use −52,020 cal.

For the solubility of lead dioxide in 5.3 N HNO_3, Cummings[81] gave 1.4×10^{-4} moles per liter. Using 1.1 for the activity coefficient of the nitric acid and 0.1 for the lead ion, a computation gives as a rough approximation,

$$PbO_2 + 4H^+ = Pb^{+4} + 2H_2O, \qquad \Delta F^\circ = 10{,}850 \text{ cal.}$$

and for the free energy of Pb^{+4}, 72,600 cal. Hence,

$$Pb^{+2} = Pb^{+4} + 2e^-, \qquad E^\circ = \text{ca } -1.7$$

$$PbO_2 + 2H_2O = Pb^{+4} + 4OH^-, \qquad K = 10^{-64}$$

From the free energies, one calculates,

$$2OH^- + PbO(r) = PbO_2 + H_2O + 2e^-, \qquad E^\circ_B = -0.250.$$

However, the half-reaction cannot be measured directly in alkaline solution because of the formation of the intermediate oxide, Pb_3O_4, and probably also Pb_2O_3. Andrews and Brown[82] gave −142,210 cal. for the free energy of formation of Pb_3O_4, and Glasstone[83] wrote,

$$Pb_2PbO_4 = 2Pb^{++} + PbO_4^{-4}, \qquad K = 5.3 \times 10^{-51}$$

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[79] Glasstone, S., J. Chem. Soc., **121**, 1456 and 1469 (1922).

[80] Andrews, L. V., and Brown, D. J., J. Am. Chem. Soc., **56**, 388 (1934).

[81] Cummings, A. C., Z. Elektrochem., **13**, 19 (1907); Trans. Faraday Soc., **2**, 197 (1908).

[82] Andrews, L. V., and Brown, D. J., J. Am. Chem. Soc., **56**, 389 (1934).

[83] Glasstone, S., J. Chem. Soc., **121**, 1469 (1922).

Grube[84] stated that both PbO_3^{--} and $Pb(OH)_6^{--}$ are present in alkaline solution and gave,

$$2OH^-(8.4\ N) + PbO_2^{--} = PbO_3^{--} + H_2O + 2e^-, \qquad E_B^\circ = -0.208$$

This would appear to correspond to an E° of about -0.28 and this was approximately the figure estimated by Glasstone.

Elbs and his co-workers[85] prepared plumbic sulfate by the electrolysis of sulfuric acid (density 1.8) with a lead anode, and plumbic dichromate $Pb(Cr_2O_7)_2$ by a similar process, using concentrated chromic acid. With phosphoric acid they prepared $Pb(H_2PbO_4)_4$. The electrolysis of 100 per cent acetic acid yields the plumbic acetate, $Pb(C_2H_3O_2)_4$. By the action of cold concentrated hydrochloric acid upon the dioxide, the tetrachloride and the chloroplumbic acid, H_2PbCl_6, have been formed. There are no thermodynamic data for any of these plumbic compounds.

TABLE 26

CONSTANTS FOR THE EQUATION EXPRESSING THE E.M.F. OF THE LEAD STORAGE BATTERY AS A FUNCTION OF TEMPERATURE

$M H_2SO_4$	$E_{0^\circ C.}$	$a \times 10^6$	$b \times 10^8$
1	1.9174	56.1	108
2	1.9664	159	103
3	2.0087	178	97
4	2.0479	177	91
5	2.0850	167	87
6	2.1191	162	85
7	2.1507	153	80

The lead storage battery. The cell reaction in the familiar lead storage battery is, for discharge,

$$PbO_2 + Pb + 4H^+ + 2SO_4^{--} = 2PbSO_4 + 2H_2O.$$

The E° potential for the reaction may be obtained from the two half-reaction potentials given above, but as the cell operates at fairly high acid (density H_2SO_4, 1.2 to 1.3 when charged) the experimental values for the electromotive force are more significant. Harned and Hamer have represented these electromotive forces for the temperature range of 0° to 60° C. by the equation,

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[84] Grube, G., Z. Elektrochem., **28**, 285 (1922).

[85] Elbs, K., and Fischer, F., Z. Elektrochem., **7**, 343 (1900); Elbs, K., and Nübling, R., Z. Elektrochem., **9**, 776 (1903).

$$E = E_{0^\circ} + at + bt^2.$$

The constants for the equation are summarized in Table 26 for various molal concentrations of sulfuric acid. Although many theories have been proposed, little is actually known regarding the mechanism of the two-electron transfer which occurs at the lead dioxide plate.

CHAPTER IX

Gallium, Indium, and Thallium

The elements gallium, indium, and thallium resemble boron and aluminum in having two *s* electrons and one *p* electron in their valence shell. However, their important chemical properties are largely those of their +3 ions, and these ions are unlike boron and aluminum in that they do not have the noble gas structure but are of the so-called "eighteen electron" type. For this reason these elements will be discussed as a separate group.

Gallium

The standard state of the element is the solid metal. From the heat of formation, 52.0 kcal., chosen by Bichowsky and Rossini, and the entropy of formation, 29.8 cal. per degree, the free energy of formation of Ga(g) is 43.2 kcal.

Oxidation states. The principal oxidation state is +3, which is represented by the ion, Ga^{+++}, in acid solution and $H_2GaO_3^-$ in alkaline solution. Halides of the +2 state may be prepared; and, since the positive ion has one *s* electron still remaining in the outer shell, it may double up to form an ion, Ga_2^{+4}, like mercurous, in which the two electrons constitute a bond holding the two gallium atoms together. The +1 oxide, Ga_2O, is formed by the reduction of the +3 oxide by the metal at high temperatures.

The gallium-gallic ion couple. Schwarz von Bergkampf[1] reports for the gallium-gallic ion couple by direct cell measurement,

$$Ga = Ga^{+++} + 3e^-, \qquad E^\circ = 0.52$$

The corresponding free energy of formation is −36,000 cal. This potential is in fair agreement with the work of Richards and Boyer.[2] Schwarz von Bergkampf also measured the heat of solution of the metal in 9 *N* hydrochloric acid and found −32,000 cal., which leads to −23.2 cal. per degree for the entropy of Ga^{+++} in this solution. The entropy at the heat content of the infinitely dilute solution is certainly, at most, -50; hence there is either a very large heat of dilution or the gallium is not present in the form of the $+3$ ion.

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[1] Schwarz von Bergkampf, E., Z. Elektrochem., **38**, 847 (1932).

[2] Richards, T. W., and Boyer, S., J. Am. Chem. Soc., **43**, 274 (1921).

Fricke and Meyring[3] have given the following data:

$$\mathrm{GaOH^{++} = Ga^{+++} + OH^-}, \qquad K = 4 \times 10^{-12}$$

$$\mathrm{Ga(OH)_2^+ = GaOH^{++} + OH^-}, \qquad K = 1.6 \times 10^{-11}$$

$$\mathrm{HGaO_3^{--} = GaO_3^{---} + H^+}, \qquad K = 2 \times 10^{-12}$$

$$\mathrm{H_2GaO_3^- = HGaO_3^{--} + H^+}, \qquad K = 4.8 \times 10^{-11}$$

Although it is difficult to make an accurate combination of these values with the solubility of the hydroxide in acids and bases as given by Porter and Browning[4] and by Fricke and Blencke,[5] we shall write as approximate values for the freshly precipitated hydroxide,

$$\mathrm{Ga(OH)_3(s) = Ga^{+++} + 3OH^-}, \qquad K = \text{ca } 5 \times 10^{-37}$$

$$\mathrm{H_3GaO_3(s) = H_2GaO_3^- + H^+}, \qquad K = \text{ca } 1 \times 10^{-15}.$$

Hence, the free energy of $Ga(OH)_3$ is ca $-198{,}300$ cal.; and $H_2GaO_3^-$, ca $-178{,}000$ cal.; and the potential in alkaline solution,

$$\mathrm{4OH^- + Ga = H_2GaO_3^- + H_2O} + 3e^-, \qquad E_B^\circ = \text{ca } 1.22$$

The metal dissolves readily in both acids and alkalies with the evolution of hydrogen.

The heat of combustion of the metal to form Ga_2O_3 is given as -255.8 kcal. Estimating the entropy of the oxide as 24 gives ΔS°, -70 cal. per degree, and ΔF° of formation, $-235{,}000$ cal. The free energy of hydration then is 8500 cal. However, upon standing, the hydroxide goes over to a less soluble modification and the free energy of hydration to give this form is probably negative.

Gallous chloride. De Boisbaudran[6] has studied the preparation and properties of the dichloride, $GaCl_2$, or probably Ga_2Cl_4. The chloride may be prepared at high temperatures, and it is soluble in a small amount of water without decomposition, but the solution evolves hydrogen upon dilution. Also the chloride is said to be formed in solution by treating a concentrated solution of the gallic chloride with the metal. Upon dilution this solution evolves hydrogen. These facts indicate that the chloride is slightly dissociated in concentrated chloride solution, and that the undissociated chloride does not decompose water. These facts are consistent with the following potentials:

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[3] Fricke, R., and Meyring, K., Z. anorg. allgem. Chem., **176**, 329 (1928).

[4] Porter, L. E., and Browning, P. E., J. Am. Chem. Soc., **41**, 1491 (1919).

[5] Fricke, R., and Blencke, W., Z. anorg. allgem. Chem., **143**, 184 (1925).

[6] De Boisbaudran, L., Compt. rend., **82**, 1098 (1876); *ibid.*, **83**, 636 and 824 (1876).

$$Ga^{++} = Ga^{+++} + e^-, \qquad E^\circ = \text{ca } 0.65$$

$$Ga = Ga^{++} + 2e^-, \qquad E^\circ = \text{ca } 0.45$$

In the absence of a high concentration of chloride ion, the oxidation of Ga^{++} by water must be very rapid. The +2 state in alkaline solution appears to be unstable with respect to the decomposition into gallate and the metal. The free energy of Ga^{++} is ca −21,000 cal.

The +1 oxide. The heat of formation of the +1 oxide, Ga_2O, has been determined by Klemm and Schnick[7] as −82 kcal. Estimating the entropy of the oxide as 22 cal. per degree, the ΔS° of formation is −22.9 and ΔF°, −75,200 cal.

$$H_2O + 2Ga = Ga_2O + 2H^+ + 2e^-, \qquad E^\circ = 0.4$$

$$2H_2O + Ga_2O = Ga_2O_3 + 4H^+ + 4e^-, \qquad E^\circ = 0.5$$

These potentials are not very significant, as the relative solubilities of the two oxides in acids are not known. They do show, however, that the +1 oxide is unstable with respect to its decomposition into the +3 oxide and the metal.

Indium

The standard state of the element is the metal. The free energy of the monatomic gas, In(g), may be computed from the heat of sublimation, 52 kcal., and the entropy of sublimation, 27 cal. per degree. The value is 44 kcal.

Oxidation states. The only ion stable in water solutions is the In^{+++}. The halides of the +1 and +2 states may be prepared and the probable potentials of the In^+ and In^{++} or In_2^{+4} ions will be discussed.

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[7] Klemm, W., and Schnick, I., Z. anorg. allgem. Chem., **226**, 353 (1936).

The indium-indic ion couple. From the precise work of Hattox and De Vries[8] on the direct measurement of the indium-indic ion electrode in sulfate solutions, the following potential is obtained,

$$\mathrm{In} = \mathrm{In}^{+++} + 3e^-, \qquad E^\circ = 0.340.$$

The free energy of In^{+++} then is −23,500 cal. The same authors found for the first step in the hydrolysis of the ion,

$$\mathrm{In}^{+++} + \mathrm{H_2O} = \mathrm{InOH}^{++} + \mathrm{H}^+, \qquad K = 2 \times 10^{-4}$$

so even in the absence of excess acid, the principal constituent in solutions of indic sulfate is the unhydrolyzed ion. There are no data on the free energy or the solubility of indium hydroxide. Ditte's[9] value for the heat of formation of the oxide, In_2O_3, is −240 kcal. Estimating the entropy of the oxide as 29, the entropy of formation is −73.5 cal. per degree, and the free energy, −218,000 cal. The oxide is not appreciably soluble in hydroxide; hence one may write,

$$6\mathrm{OH}^- + 2\mathrm{In} = \mathrm{In_2O_3} + 3\mathrm{H_2O} + 6e^-, \qquad E_B^\circ = 1.18.$$

This potential is not very significant, however, as the oxidation of the metal in alkaline solution would certainly form the hydroxide. The metal dissolves fairly readily in acid solutions and probably slowly in alkalies with the evolution of hydrogen.

The +1 and +2 oxidation states. The chlorides, InCl and $InCl_2$ or In_2Cl_4, may be prepared by the action of chlorine on the metal. From the reactions of these chlorides with hot water, as recorded by Thiel,[10] the following decompositions occur:

$$2\mathrm{In}^{++} = \mathrm{In}^{+++} + \mathrm{In}^+$$

$$2\mathrm{In}^+ = \mathrm{In}^{++} + \mathrm{In}$$

To account for these reactions, the approximate potentials must be,

$$\mathrm{In}^{++} = \mathrm{In}^{+++} + e^-, \qquad E^\circ = \text{ca } 0.45$$

$$\mathrm{In}^{+} = \mathrm{In}^{++} + e^-, \qquad E^\circ = \text{ca } 0.35$$

$$\mathrm{In} = \mathrm{In}^{+} + e^-, \qquad E^\circ = \text{ca } 0.25$$

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[8] Hattox, E. M., and De Vries, T., J. Am. Chem. Soc., **58**, 2126 (1936).
[9] Ditte, A., Compt. rend., **72**, 858 (1871).
[10] Thiel, A., Z. anorg. Chem., **39**, 119 (1904); *ibid.*, **40**, 280 (1904).

for the following reasons. The sum of the three E° values must be 3×0.340 from the In—In^{+++} potential. In order to account for the decompositions, the E° for the first couple must be greater than that for the second, and similarly the second must be greater than the third. The value of the third can hardly be negative since the metal dissolves readily in acid. As a check on this last point the free energy of InCl may be calculated from the thermal data. Bichowsky and Rossini select −44.6 kcal. as the heat of formation. Taking the entropy of InCl as 23.2 in comparison with 23.0 for silver chloride, the entropy of formation is 18.0 cal. per degree and the free energy −39,200 cal. Hence,

$$Cl^- + In = InCl(s) + e^-, \qquad E^\circ = 0.34.$$

The solubility of the InCl cannot be measured; but from the relations in this region of the periodic system, it should be more soluble than TlCl but probably less than one molal. This E° value is then in approximate agreement with that chosen for the In—In^+ couple.

In the equilibrium between the metal and a solution of the ion, In^{+++}, there will be present appreciable concentrations of In^+ and In^{++}. In the absence of the metal, the ion of the lower oxidation states will rapidly disappear because of their decomposition or their oxidation by hydrogen ion. In alkaline solution the hydroxides, InOH and $In(OH)_2$, are unstable with respect to the formation of the less soluble $In(OH)_3$ and the metal.

Thallium

The standard state of thallium is the solid metal, Tl(α). There is a transition to the β form at 235.3° C. From a number of rather discordant values, Bichowsky and Rossini pick 40 kcal. as the heat of sublimation. Using 27.7 as the entropy of sublimation, the free energy of Tl(g) is 31,700 cal. Randall[11] gives the free energy at 25° C. of Tl(β) as 39 cal.

Oxidation states. Thallium forms compounds of the +1 oxidation state, thallous, and +3 state, thallic. A very unstable +2 bromide, $TlBr_2$, may be prepared, but this state has a high free energy of decomposition into the +1 and +3 states and is essentially nonexistent, although in some cases an appreciable concentration of +2 complex ions may be present in the equilibrium between thallous and thallic.

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[11] Randall, M., International Critical Tables, VII, 251.

The thallium-thallous couple. The very precise measurements of Lewis and his co-worker[12] on the thallium-thallous ion electrode has led to the value,

$$\mathrm{Tl} = \mathrm{Tl}^+ + e^-, \qquad E^\circ = 0.3363$$

The corresponding free energy of Tl^+ is −7760 cal. Randall[13] gives,

$$\mathrm{Tl(OH)(s)} = \mathrm{Tl}^+ + \mathrm{OH}^-, \qquad \Delta F^\circ = 190 \text{ cal.}$$
$$K = 7.2 \times 10^{-1}$$

The free energy of the solid hydroxide is then −45,535 cal. and the potential of the couple in alkaline solution,

$$\mathrm{OH}^- + \mathrm{Tl} = \mathrm{Tl(OH)(s)} + e^-, \qquad E^\circ_B = 0.3445$$

The free energy of hydration of the oxide is given as

$$\mathrm{Tl_2O(s)} + \mathrm{H_2O(g)} = 2\mathrm{Tl(OH)}\ \mathrm{(s)}, \qquad \Delta F^\circ = -3880 \text{ cal.}$$

Randall also summarizes the following data:

$$\mathrm{TlCl(s)} = \mathrm{Tl}^+ + \mathrm{Cl}^-, \qquad \Delta F^\circ = 5086$$
$$K = 1.9 \times 10^{-}$$
$$\mathrm{TlBr(s)} = \mathrm{Tl}^+ + \mathrm{Br}^-, \qquad \Delta F^\circ = 7420$$
$$K = 3.6 \times 10^{-6}$$
$$\mathrm{TlI(s)} = \mathrm{Tl}^+ + \mathrm{I}^-, \qquad \Delta F^\circ = 9883$$
$$K = 5.8 \times 10^{-8}$$

The potentials for the couples involving these halides are:

$$\mathrm{Cl}^- + \mathrm{Tl} = \mathrm{TlCl(s)} + e^-, \qquad E^\circ = 0.557$$
$$\mathrm{Br}^- + \mathrm{Tl} = \mathrm{TlBr(s)} + e^-, \qquad E^\circ = 0.658$$
$$\mathrm{I}^- + \mathrm{Tl} = \mathrm{TlI(s)} + e^-, \qquad E^\circ = 0.765$$

and the corresponding free energies: TlCl, −44,190 cal.; TlBr, −39,750 cal.; TlI, −29,976 cal. These values are in remarkably good agreement with those calculated from the heats of formation and the entropies of formation by the Third Law of Thermodynamics.

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[12] Cf. Lewis, G. N., and Randall, M., *Thermodynamics* (McGraw-Hill, New York, 1923), p. 412.

[13] Randall, M., International Critical Tables, VII, 251.

Kolthoff[14] has given for the solubility product of thallous sulfide,

$$Tl_2S = 2Tl^+ + S^{--}, \qquad K = 1.2 \times 10^{-24}$$

One then calculates for the Tl—Tl_2S couple,

$$S^{--} + 2Tl = Tl_2S + 2e^-, \qquad E^\circ_B = 1.04.$$

For thallous iodate, Spencer[15] wrote for the product of the concentrations,

$$TlIO_3 = Tl^+ + IO_3^-, \qquad K = 4.5 \times 10^{-6}.$$

Noyes and Abbot[16] studied equilibria between a number of thallous salts at 40° C. The following are values for the concentration products at that temperature.

$$TlBrO_3 = Tl^+ + BrO_3^-, \qquad K = 3.9 \times 10^{-4}$$

$$TlCNS = Tl^+ + CNS^-, \qquad K = 5.8 \times 10^{-4}$$

The thallous-thallic couple. Noyes and Garner[17] measured the oxidation potential of the thallous-thallic couple in nitric acid solutions and gave −1.230 as the E° value. Partington and Stonehill[18] have measured the same potential in sulfuric acid at 25° C. and deduce −1.2207 as the true value. Sherrill and Haas[19] chose perchloric acid as the electrolyte because of the freedom from complex formation of the perchlorate and have expressed their E° value as a function of the total ionic strength of the cell.

$$E^\circ = 1.2466 + 0.0076\,u + 0.00482\,u^2$$

These authors point out that the extrapolation to zero ionic strength in their measurements is large, but in the absence of a better value, we shall write,

$$Tl^+ = Tl^{+++} + 2e^-, \qquad E^\circ = -1.25.$$

This would make the free energy of thallic ion, Tl^{+++}, 49,750 cal. The same authors estimate the solubility product of thallic hydroxide to be 1.5×10^{-44}. Hence one computes for the free energy of the hydroxide, $Tl(OH)_3(s)$, −123,000 cal. This gives for the potential of the thallous-thallic couple in alkaline solution,

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[14] Kolthoff, I. M., J. Phys. Chem., **35**, 2720 (1931).

[15] Spencer, J. F., Z. physik. Chem., **80**, 707 (1912).

[16] Noyes, A. A., and Abbot, C. G., Z. physik. Chem., **16**, 130 (1895).

[17] Noyes, A. A., and Garner, C. S., J. Am. Chem. Soc., **58**, 1268 (1936).

[18] Partington, J. R., and Stonehill, H. I., Trans. Faraday Soc., **31**, 1365 (1935).

[19] Sherrill, M. S., and Haas, A. J., Jr., J. Am. Chem. Soc., **58**, 953 (1936).

$$2OH^- + TlOH(s) = Tl(OH)_3(s) + 2e^-, \qquad E_B^\circ = 0.05$$

In neutral solution thallous sulfate may be oxidized, on a platinum anode, quantitatively to the thallic hydroxide by using a fairly high overvoltage. At lower voltages a black form of the oxide Tl_2O_3 is said to form, and the same product is obtained in hot alkaline solutions. In slightly acid solutions of the thallous sulfate, Gallo and Ceuni[20] report the anodic oxidation to a peroxide complex, Tl_3O_5.

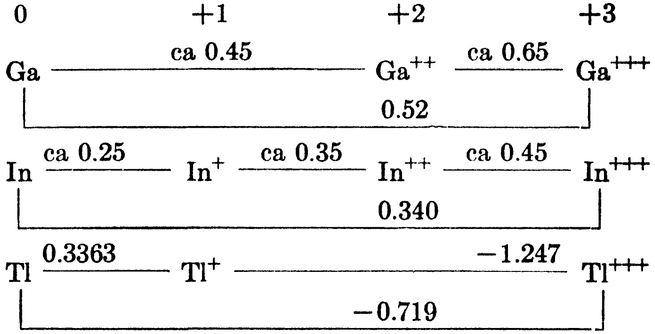
Because of the slight solubility of the thallous chloride, the net reaction for the thallous-thallic couple in the presence of chloride may be written as,

$$TlCl = Tl^{+++} + Cl^- + 2e^-, \qquad E^\circ = -1.36$$

This value, for practical purposes, is too low, as the chloride certainly forms complex ions with the thallic. Chloride ion does not readily reduce thallic solutions, as the potential indicates, but the reduction, of course, occurs with bromide and iodide.

Summary of Group 3′ potentials. For comparison of the potentials of the three elements of the group, the values for the various couples in acid solution are summarized in the following scheme:

ACID SOLUTION



The principal point of interest is the increase in the oxidizing power of the +3 ion with increasing atomic weight. The increasing stability of the +1 state and the decreasing stability of the +2 state may also be noted.

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[20] Gallo, G., and Ceuni, G., Gass. chim. Ital., **39**, 285 (1908).

CHAPTER X

Zinc, Cadmium, and Mercury

Like the alkaline earths, the elements of this group have two *s* electrons in their valence shell, but they are unlike the alkaline earth elements in that the kernels are of the 18-electron type instead of octets. Mercury forms -ous compounds in which the mercury atom has lost only one of the *s* electrons; and, as a result, two such atoms combine to form a double ion with an electron pair bond, for example, $Hg{:}Hg^{++}$.

Zinc

The standard state of the element is the solid metal. Overstreet[1] has made a careful study of the thermal and vapor pressure data of zinc. He computes for the sublimation of the solid the following data: ΔH°, 31,189 cal.; ΔS°, 38.46 cal. per degree; and ΔF°, 22,692 cal. The gas is monatomic.

Oxidation states. Zinc forms compounds in which the oxidation state is +2. There appears to be no reliable evidence for the existence of the +1 state.

The zinc-zinc ion couple. Shrawder, Cowperthwaite, and La Mer[2] reviewed the previous work on the zinc electrode and calculate

$$Zn = Zn^{++} + 2e^-, \qquad E^\circ = 0.7620$$

The free energy of zinc ion is −35,176 cal.

Dietrich and Johnston[3] report for the zinc-zinc hydroxide electrode against the mercury-mercuric oxide electrode in alkali,

$$Zn + HgO + H_2O = Zn(OH)_2 + Hg(l), \qquad E^\circ = 1.3438$$

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[1] Overstreet, R., (Thesis, University of California, 1930). Cf. Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).

[2] Shrawder, J., Cowperthwaite, I. A., and La Mer, V. K., J. Am. Chem. Soc., **56**, 2348 (1934).

[3] Dietrich, H. G., and Johnston, J., J. Am. Chem. Soc., **49**, 1419 (1927).

This gives,

$$2OH^- + Zn = Zn(OH)_2(s) + 2e^-, \quad E^\circ_B = 1.245$$

and

$$Zn(OH)_2(s) = Zn^{++} + 2OH^-, \qquad K = 4.5 \times 10^{-17}.$$

There are several unstable forms of zinc hydroxide, and these authors carefully prepared the stable orthorhombic crystalline modification for their work. From their value of the solubility product and the measured solubility, 1×10^{-6} M, it appears that the saturated solution contains considerable un-ionized zinc hydroxide. The free energy of the solid hydroxide is −132,640 cal. as calculated from these potentials. Based on the heat of formation of −153,500 cal. and the entropy of formation of −72.3 cal. per degree, assuming the entropy of $Zn(OH)_2$ is 18, the free energy is −131,900 cal., in fair agreement with the potential value.

Kolthoff and Kameda[4] found for the hydrolysis of zinc ion,

$$Zn^{++} + H_2O = Zn(OH)^+ + H^+, \qquad K = 2.45 \times 10^{-10}$$

Their value for the solubility product, 1×10^{-17}, is in approximate agreement with that given above.

From the solubility of the hydroxide in alkali, Dietrich and Johnston calculate,

$$Zn^{++} + 4OH^- = ZnO_2^{--} + 2H_2O, \qquad \Delta F^\circ = -21{,}090 \text{ cal.}$$

$$K = 2.8 \times 10^{15}$$

$$Zn(OH)_2 = ZnO_2^{--} + 2H^+, \qquad K = 1.0 \times 10^{-29}$$

This makes the free energy of zincate ion, ZnO_2^{--}, −93,030 cal., and the potential of the zinc-zincate couple

$$4OH^- + Zn = ZnO_2^{--} + 2H_2O + 2e^-, \quad E^\circ_B = 1.216$$

There are surprisingly few data on the zinc ammonia complex ion. For the dissociation,

$$Zn(NH_3)_4^{++} = Zn^{++} + 4NH_3(aq)$$

Euler[5] gives 2.6×10^{-10} from electromotive force measurements, and Wijs,[6] gives 9.8×10^{-10} from the partial pressure of ammonia over solutions of the complex ion. The latter appears to be the more reliable. Hence the free energy of formation of the ion $Zn(NH_3)_4^{++}$ is −72,740 cal. and for the half-reaction,

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[4] Kolthoff, I. M., and Kameda, T., J. Am. Chem. Soc., **53**, 835 (1931).

[5] Euler, H., Ber., **36**, 3400 (1903).

$$4NH_3(aq) + Zn = Zn(NH_3)_4^{++} + 2e^-, \qquad E_B^\circ = 1.03.$$

Euler also determined the dissociation constant of the complex cyanide, $Zn(CN)_4^{--}$ and found $K = 1.3 \times 10^{-17}$. Kunschert[7] gave 1.287 as the E° value of the zinc–complex cyanide couple which corresponds to 1.2×10^{-18} for the constant. He assumed the formula of the ion to be $Zn(CN)_3^{--}$. We shall write,

$$4CN^- + Zn = Zn(CN)_4^{--} + 2e^-, \qquad E^\circ = 1.26.$$

Kunschert measured the potential of the zinc–complex oxalate couple. Attempting to recalculate his results, we find the dissociation constant approximately $K = 10^{-9}$ and the potential of the couple,

$$3C_2O_4^{--} + Zn = Zn(C_2O_4)_3^{-4} + 2e^-, \qquad E^\circ = \text{ca } 1.02.$$

The heat of formation of zinc sulfide is given as −44,300 cal. and the entropy of formation is −3.8 cal. per degree. Based on these values, the free energy of formation is −43,200 cal. and the potential of the zinc-zinc sulfide couple

$$S^{--} + Zn = ZnS + 2e^-, \qquad E_B^\circ = 1.44.$$

The free energy enables us to calculate the solubility product of zinc sulfide.

$$ZnS = Zn^{++} + S^{--}, \qquad \Delta F^\circ = 31{,}620 \text{ cal.}$$

$$K = 4.5 \times 10^{-24}$$

This figure is probably as reliable as any of the direct experimental values.

Kelley and Anderson[8] in their study of the carbonate data give

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[6] Wijs, H. J. de, Rec. trav. chim., **44**, 663 (1925).

[7] Kunschert, F., Z. anorg. Chem., **41**, 341 (1904).

[8] Kelley, K. K., and Anderson, C. T., U. S. Bur. Mines Bull., No. 384 (1935).

$-174{,}780$ cal. for the free energy of formation of zinc carbonate. Making use of the free energies of the ions, one calculates

$$ZnCO_3 = Zn^{++} + CO_3^{--}, \qquad \Delta F^\circ = 13{,}220 \text{ cal.}$$
$$K = 2 \times 10^{-10}$$

The heat of formation of the carbonate is subject to some uncertainties; hence too much weight cannot be given to this value for the constant. Ageno and Valla[9] gave 2.1×10^{-11} as the solubility product. Taking 6×10^{-11} as an average,

$$CO_3^{--} + Zn = ZnCO_3 + 2e^-, \qquad E_B^\circ = 1.07$$

In both acidic and basic solution, the zinc couple is more positive than the corresponding hydrogen couple, although the difference is smaller in the basic solution. However, because of the very high overvoltage of hydrogen on zinc the metal does not dissolve rapidly in hydrogen ion unless it is in contact with some substance on which hydrogen gas can be liberated at a lower overvoltage. Likewise, because of the overvoltage, zinc ion or zincate may be reduced to the metal in water solutions and both the voltage and overvoltage are more favorable at low hydrogen-ion concentration. The quantitative estimation of zinc by cathodic precipitation may be made in a solution buffered by acetate and acetic acid, but the determination is more satisfactory when the electrolyte is zincate or the complex cyanide.

Cadmium

The standard state of cadmium is the solid metal. Kelley[10] calculates 18,489 cal. as the free energy of sublimation from vapor pressure and specific heat data. For the heat and entropy of sublimation, he gave ΔH°, 26,754 cal.; and ΔS°, 40.07 cal. per degree. The gas is monatomic.

Oxidation states. Like zinc, the only important oxidation state is the $+2$. The hydroxide is considerably more basic than zinc hydroxide. There is some evidence for the existence of the $+1$ oxide, Cd_2O, and chloride, Cd_2Cl_2.

The cadmium-cadmium ion couple. Harned and Fitzgerald[11] have reviewed the literature on the cadmium-cadmium ion couple and give,

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[9] Ageno, F., and Valla, E., Atti. Accad. Lincei, **20**, 705 (1911).
[10] Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).
[11] Harned, H., and Fitzgerald, M. E., J. Am. Chem. Soc., **58**, 2624 (1936).

$$\mathrm{Cd} = \mathrm{Cd}^{++} + 2e^-, \qquad E^\circ = 0.4020$$

This corresponds to −18,550 cal. for the free energy of the ion, Cd^{++}.

From measurements on the cell whose reaction is,

$$\mathrm{Cd} + \mathrm{HgO} + \mathrm{H_2O} = \mathrm{Cd(OH)_2} + \mathrm{Hg},$$

Ishikawa and Shibata[12] obtained −42,100 for the free energy of the reaction and calculated for the solubility product, $K = 1.17 \times 10^{-14}$. Wijs[13] reported 2.8×10^{-14} and 2.1×10^{-14}. We shall write ΔF° (formation $Cd(OH)_2$) = −112,730 cal.

$$\mathrm{Cd(OH)_2} = \mathrm{Cd}^{++} + 2\mathrm{OH}^-, \qquad K = 1.2 \times 10^{-14}$$

$$2\mathrm{OH}^- + \mathrm{Cd} = \mathrm{Cd(OH)_2} + 2e^-, \qquad E_B^\circ = 0.815$$

There appears to be no appreciable formation of cadmate ion in dilute hydroxide solutions. The solubility of the hydroxide in water is 1.4×10^{-5} molal, so from the activity product given above, the hydroxide which dissolves is not completely ionized.

For the dissociation constant of the cadmium-ammonia complex ion, Wijs[14] reported 2.5×10^{-7}, and Euler[15], 1×10^{-7}. The latter is from e.m.f. measurements of a cell with no correction for the activity coefficients, while the former is from the partial pressure of ammonia over a solution of the complex ion and is probably the more reliable. Based on this value, the free energy of $Cd(NH_3)_4^{++}$ is −52,850 cal. and

$$4\mathrm{NH_3} + \mathrm{Cd} = \mathrm{Cd(NH_3)_4^{++}} + 2e^-, \qquad E_B^\circ = 0.597$$

Euler[16] found 1.4×10^{-17} for the dissociation constant of the cyanide complex ion. The corresponding free energy of the ion, $Cd(CN)_4^{--}$, is 111,000 cal., and one computes for the potential of the couple,

$$4\mathrm{CN}^- + \mathrm{Cd} = \mathrm{Cd(CN)_4^{--}} + 2e^-, \qquad E_B^\circ = 0.90$$

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[12] Ishikawa, F., and Shibata, E., Science Rep. Tohoku Imp. Univ., **21**, 499 (1932).

[13] Wijs, H. J. de, Rec. trav. chim., **44**, 663 (1925).

[14] Wijs, H. J. de, *ibid.*

[15] Euler, H., Ber., **36**, 3400 (1903).

[16] Euler, H., *ibid.*

The same author[17] reported 4×10^{-8} for the dissociation constant of the complex thiosulfate which he considered to be $Cd(S_2O_3)_4^{-6}$. However, there may be some question as to the validity of this work.

From the heat of formation of the sulfide, −34,600 cal., and the entropy of formation, −4.9 cal. per degree (using CdS, 15, estimated), the free energy of formation is found to be −33,100 cal. This gives for the solubility product,

$$CdS = Cd^{++} + S^{--}, \qquad K = 1.4 \times 10^{-28}$$

and for the potential of the cadmium-cadmium sulfide couple,

$$S^{--} + Cd = CdS + 2e^-, \qquad E_B^\circ = 1.23.$$

Since the potential required to oxidize cadmium sulfide to the ion and free sulfur is of interest for many analytical procedures, that value will be given here although it belongs under the sulfur potentials.

$$CdS = Cd^{++} + S + 2e^-, \qquad E^\circ = -0.31$$

A fairly powerful oxidizing agent is thus required to effect the oxidation.

For the free energy of cadmium carbonate we may employ the value calculated by Kelley,[18] −163,410 cal. Making use of the free energies of the ions, one computes,

$$CdCO_3 = Cd^{++} + CO_3^{--}, \qquad \Delta F^\circ = 18{,}470 \text{ cal.}$$

$$K = 2.5 \times 10^{-14}.$$

For the cadmium-cadmium carbonate couple,

$$CO_3^{--} + Cd = CdCO_3 + 2e^-, \qquad E_B^\circ = 0.80.$$

Cadmium forms a complex ion with iodide, CdI_4^{--}. The dissociation constant has been studied by a number of investigators. Bates and Vosburgh[19] found

$$CdI_4^{--} = Cd^{++} + 4I^-, \qquad K = \text{ca } 5 \times 10^{-7}.$$

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[17] Euler, H., Ber., **37**, 1704 (1904).

[18] Kelley, K. K., and Anderson, C. T., U. S. Bur. Mines Bull., No. 384 (1935).

[19] Bates, R. G., and Vosburgh, W. C., J. Am. Chem. Soc., **60**, 137 (1938).

However, their electromotive force data could also be interpreted fairly well on the assumption that the negative ion was CdI_3^-.

The electrolytic reduction of cadmium is best accomplished from a solution of the complex cyanide, and this is the basis of the quantitative procedure (cf. Treadwell and Hall[20]).

Cadmium in the +1 state. From the very meager data regarding the chemical properties of Cd_2O and Cd_2Cl_2, one concludes that the ion Cd_2^{++} is capable of reducing water readily, hence,

$$Cd_2^{++} = 2Cd^{++} + 2e^-, \qquad E^\circ > 0.6.$$

The value of the Cd—Cd^{++} couple then fixes that of the Cd—Cd_2^{++} couple as

$$2Cd = Cd_2^{++} + 2e^-, \qquad E^\circ < 0.2.$$

Mercury

The standard state of the element is the metallic liquid. Kelley[21] has summarized the data on the vapor pressure of liquid mercury and selects the following values for the formation of the monatomic gas from the liquid: ΔH°, 14,535 cal.; ΔF°, 7590 cal.; ΔS°, 23.3 cal. per degree.

Oxidation states. Mercury forms compounds of the double mercurous ion, Hg_2^{++}, +1 oxidation state, and the mercuric ion, Hg^{++}, +2 state. Even at very low concentrations, the aqueous mercurous ion appears to be undissociated.

The mercury-mercurous ion couple. Lewis and Randall give for the mercury-mercurous ion couple,

$$2Hg = Hg_2^{++} + 2e^-, \qquad E^\circ = -0.7986.$$

Various investigators (cf. Bray and Hershey[22]) give values which vary by 0.001 volts, depending upon the extrapolation of the experimental potentials to infinite dilution. The free energy of mercurous ion corresponding to the E° is 36,850 cal. The couple is capable of rapidly attaining equilibrium and when used as an electrode is readily reversible.

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[20] Treadwell, F. P., and Hall, W. T., *Analytical Chemistry* (Wiley, New York, 1935), **2**, 197.

[21] Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).

[22] Bray, W. C., and Hershey, A. V., J. Am. Chem. Soc., **56**, 1889 (1934).

Although mercurous oxide may be prepared, it is unstable with respect to the decomposition into mercury and mercuric oxide. However, we may use the third law to calculate an approximate value for its free energy. The heat of formation is given by Bichowsky and Rossini as −21,600 cal. The entropy of the oxide has not been determined, but an estimated value of 32 cal. per degree is probably fairly close. Hence the entropy of formation is −29.5 and the free energy of formation, −12,800 cal. The solubility product corresponding to this free energy is

$$Hg_2O + H_2O = Hg_2^{++} + 2OH^-, \qquad \Delta F^\circ = 31{,}170 \text{ cal.}$$
$$K = 1.6 \times 10^{-23}$$

and the potential of the mercury-mercurous oxide couple,

$$2OH^- + 2Hg = Hg_2O + H_2O + 2e^-, \qquad E^\circ_B = -0.123.$$

Anticipating our value for the free energy of mercuric oxide, the free energy of decomposition of mercurous oxide is

$$Hg_2O = HgO(\text{red}) + Hg, \qquad \Delta F^\circ = -1140 \text{ cal.}$$

The small value of this free energy is in agreement with the fact that the decomposition of the solid is not rapid unless it is in contact with an alkaline solution.

The mercury-mercurous halide couples. Randall and Young[23] give for the mercury-mercurous chloride couple,

$$2Cl^- + 2Hg = Hg_2Cl_2 + 2e^-, \qquad E^\circ = -0.2676.$$

These authors studied the effect of oxygen upon the potential and found that in the presence of air the potential is at least a millivolt lower. This error applies also to the decinormal and normal potassium chloride calomel electrodes which have been so widely used as reference couples. Their values for these electrodes are:

DN: in air, −0.3354; absence of air, −0.3341,

N: in air, −0.2825; absence of air, −0.2812.

The free energy of formation of mercurous chloride, Hg_2Cl_2, is −50,310 cal. and the solubility product,

$$Hg_2Cl_2 = Hg_2^{++} + 2Cl^-, \qquad K = 1.1 \times 10^{-18}.$$

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[23] Randall, M., and Young, L. E., J. Am. Chem. Soc., **50**, 989 (1928).

Ishikawa and Ueda[24] report −42,700 cal. for the free energy of formation of mercurous bromide which is in exact agreement with the value selected by Randall.[25]

$$2Br^- + 2Hg = Hg_2Br_2 + 2e^-, \qquad E^\circ = -0.1397$$

The solubility product of the salt is,

$$Hg_2Br_2 = Hg_2^{++} + 2Br^-, \qquad K = 5.2 \times 10^{-23}.$$

Bates and Vosburgh[26] found for the potential of the mercury-mercurous iodide couple,

$$2I^- + 2Hg = Hg_2I_2 + 2e^-, \qquad E^\circ = 0.0405.$$

One then computes for the solubility product,

$$Hg_2I_2 = Hg_2^{++} + 2I^-, \qquad K = 4.5 \times 10^{-29}.$$

Our value for the free energy of mercurous iodide then is −26,530 cal.

Additional mercury-mercurous salt couples. Brodsky[27] has determined the solubility product of mercurous carbonate. His value and the corresponding potential are:

$$CO_3^{--} + 2Hg = Hg_2CO_3 + 2e^-, \qquad E^\circ_B = -0.32$$

$$Hg_2CO_3 = Hg_2^{++} + CO_3^{--}, \qquad K = 9.0 \times 10^{-17}.$$

The potential of the mercury-mercurous sulfate couple,

$$SO_4^{--} + 2Hg = Hg_2SO_4 + 2e^-, \qquad E^\circ = -0.6151$$

is given by Harned and Hamer.[28] Using our value for the $Hg—Hg_2^{++}$ couple, the solubility product is,

$$Hg_2SO_4 = Hg_2^{++} + SO_4^{--}, \qquad K = 6.2 \times 10^{-7}.$$

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[24] Ishikawa, F., and Ueda, Y., Science Rep. Tohoku Imp. Univ., **22**, 249 (1933).

[25] Randall, M., International Critical Tables, **VII**, 260.

[26] Bates, R. G., and Vosburgh, W. C., J. Am. Chem. Soc., **59**, 1189 (1937).

[27] Brodsky, A. E., Z. Elektrochem., **35**, 837 (1929).

[28] Harned, H. S., and Hamer, W. J., J. Am. Chem. Soc., **57**, 31 (1935).

Brodsky[29] recalculates the work of a number of early investigators to give the following approximate values for the solubility products:

	K	$E°$
Hg_2CrO_4	2×10^{-9}	-0.54
$Hg_2C_4H_4O_6$	1×10^{-10}	-0.50
$Hg_2C_2O_4$	1×10^{-13}	-0.41
$Hg_2(CH_3COO)_2$	2×10^{-15}	-0.36
$Hg_2(IO_3)_2$	1.3×10^{-18}	-0.27
$Hg_2(CNS)_2$	3×10^{-20}	-0.22
$Hg_2(CN)_2$	5×10^{-40}	0.36
Hg_2S	10^{-45}	0.53

The corresponding $E°$ values have been calculated, but they are to be considered merely as approximations.

The mercurous-mercuric couple. Carter and Robinson[30] measured the potential of the mercurous-mercuric couple in perchloric acid against a calomel electrode at 18° C. and reported $E°$, -0.913. Popoff and his co-workers[31] have also measured the potential of the couple in perchloric acid, using a hydrogen electrode. They found $E° = -0.905$. The extrapolation of the measured potentials to infinite dilution would appear to give a slightly lower value, and we shall write

$$Hg_2^{++} = 2Hg^{++} + 2e^-, \qquad E° = -0.910$$

From this value one computes for the free energy of mercuric ion 39,415 cal., and for the equilibrium between mercury, mercuric, and mercurous ions,

$$Hg + Hg^{++} = Hg_2^{++}, \qquad \Delta F° = -2561 \text{ cal.}$$

$$K = 81.$$

This equilibrium is readily reversible and if the mercuric compound of a given ion is much less soluble than the corresponding mercurous compound, the latter becomes unstable with respect to the decomposition into mercury and the mercuric compound. For the mercury-mercuric couple, one calculates,

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[29] Brodsky, A. E., Z. Elektrochem., **35**, 833 (1929).

[30] Carter, S. R., and Robinson, R., J. Chem. Soc., 267 (1927).

[31] Popoff, S., Riddick, J. A., Weith, V. I., and Ough, L. D., J. Am. Chem. Soc., **53**, 1195 (1933).

$$Hg = Hg^{++} + 2e^-, \qquad E^\circ = -0.854$$

Since the Hg^{++} to Hg_2^{++} couple is a stronger oxidizing agent than the Hg^{++} to Hg couple, reducing agents will first reduce mercuric ion to mercurous, but as the value for the Hg_2^{++} to Hg couple is about the same, excess of the reducing agent will take the mercurous ion on down to mercury. It also follows from these potentials that fairly powerful oxidizing agents, such as bromine water or hot nitric acid, are required to oxidize mercurous ion to mercuric.

The mercury-mercuric oxide couple. Because of the lower solubility of mercuric oxide, it is reduced directly to mercury without the formation of mercurous oxide as an intermediate step, the equilibrium discussed above being reversed in this case. Lewis and Randall[32] give

$$Hg + 2OH^- = HgO(r) + H_2O + 2e^-, \qquad E_B^\circ = -0.0984.$$

Using our values for the free energy of water and hydroxide, we find the free energy of the oxide to be $-13{,}940$ cal. Randall[33] calculates $-13{,}950$ cal. from the data of Taylor and Hulett on the dissociation of the oxide into mercury and oxygen. The third law value, using $\Delta H^\circ = 21{,}700$ cal. and $\Delta S^\circ = -26.4$ cal. per degree, is $-13{,}820$ cal., but there are some uncertainties in both of the thermal quantities. The solubility product which corresponds to the above potential is,

$$HgO + H_2O = Hg^{++} + 2OH^-, \qquad K = 2.7 \times 10^{-26}.$$

Gerke[34] gives -0.0991 for the potential of the couple using the yellow form of the oxide. Taylor and Hulett were unable to detect a difference in the decomposition pressures of the two modifications at high temperatures. Garrett and Hirschler[35] gave

$$HgO(r) = HgO(y), \qquad \Delta F^\circ = 31 \text{ cal.}$$

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[32] Lewis, G. N., and Randall, M., *Thermodynamics* (McGraw-Hill, New York, 1923), p. 434.

[33] Randall, M., International Critical Tables, VII, 258.

[34] Gerke, R. H., Chem. Rev., **1**, 385 (1925).

[35] Garrett, A. B., and Hirschler, A. E., J. Am. Chem. Soc., **60**, 305 (1938).

The same authors found for the solubility of the oxide in hydroxide,

$$HgO + OH^- = HHgO_2^-, \qquad \Delta F^\circ = 6145 \text{ cal.}$$
$$K = 3.15 \times 10^{-5}.$$

The mercury-mercuric sulfide couple. The third law affords the most accurate method of determining the free energy of mercuric sulfide, HgS. For the black modification, Bichowsky and Rossini give −10,700 cal. as the heat of formation. Using ΔS as −6.3 cal. per degree, the free energy of formation is −8800 cal. and the solubility product,

$$HgS = Hg^{++} + S^{--}, \qquad K = 3 \times 10^{-53}.$$

Mercurous sulfide is unstable with respect to its decomposition into mercuric sulfide and mercury.

$$Hg_2S = HgS + Hg, \qquad \Delta F^\circ = -7800 \text{ cal.}$$

The potential of the mercury-mercuric sulfide couple is,

$$S^{--} + Hg = HgS + 2e^-, \qquad E^\circ = 0.70.$$

The potential required to oxidize mercuric sulfide to mercuric ion and sulfur is also of interest:

$$HgS = S + Hg^{++} + 2e^-, \qquad E^\circ = -1.05.$$

The mercuric cyanide and halide complex ions. The data of Sherrill[36] on the cyanide and halide mercuric complex ions are given in the following summarization:

	CN^-	I^-	Br^-	Cl^-
$\dfrac{(HgX_4^{--})}{(Hg^{++})(X^-)^4}$	2.5×10^{41}	1.9×10^{30}	4.3×10^{21}	9×10^{15}

From these data, the following potentials have been calculated:

$$4CN^- + Hg = Hg(CN)_4^{--} + 2e^-, \qquad E^\circ = 0.37$$
$$4I^- + Hg = HgI_4^{--} + 2e^-, \qquad E^\circ = 0.04$$
$$4Br^- + Hg = HgBr_4^{--} + 2e^-, \qquad E^\circ = -0.21$$
$$4Cl^- + Hg = HgCl_4^{--} + 2e^-, \qquad E^\circ = -0.38$$

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[36] Sherrill, M. S., Z. physik. Chem., **43**, 735 (1903); *ibid.*, 47, 103 (1904).

The corresponding free energies of formation of the complex ions are: $Hg(CN)_4^{--}$, 140,400 cal.; HgI_4^{--}, −51,150 cal.; $HgBr_4^{--}$, −88,400 cal.; and $HgCl_4^{--}$, −107,850 cal.

Estimating the entropies of $HgCl_2(s)$, $HgBr_2(s)$ and $HgI_2(s)$ as 34.5, 39.1, and 41.9, respectively, and using the Bichowsky and Rossini heats of formation, we find the free energies of the solid halides to be: $HgCl_2$, −42,200 cal.; $HgBr_2$, −38,800 cal.; and HgI_2(red), −24,000 cal. These values give fairly reasonable free energies of solution of the solids in excess of halide ion to form the complex ions in the case of HgI_4^{--} and $HgBr_4^{--}$, but the data for the $HgCl_2(s)$ and $HgCl_4^{--}$ do not appear to be compatible.

It is of interest to know the potential of the reduction of mercuric chloride solutions to mercurous chloride, but it is difficult to write an equation for the net reaction because of the complex nature of the mercuric chloride solution. Sherrill gives for the composition of the saturated solution: $HgCl_2(aq)$, 2.6×10^{-1}; $HgCl^+$, 2.7×10^{-4}; Hg^{++}, 3.5×10^{-8}; and $HgCl_4^{--}$, 1.6×10^{-6}, all in moles per liter. Using our free energy of the solid, we shall write,

$$Cl^- + \tfrac{1}{2}Hg_2Cl_2 = HgCl_2(\text{sat. sol.}) + e^-, \qquad E^\circ = -0.62.$$

Additional mercuric couples. There are not sufficient data to calculate the free energy of the complex mercuric ammonobasic salts. Franklin[37] found for the reaction,

$$HgNH_2Cl + NH_4^+ + Cl^- = Hg(NH_3)_2Cl,$$

that equilibrium was established at 0.49 *N* ammonium chloride. The whole problem of the free energies of these chlorides and other salts should be investigated by third law methods.

Drucker[38] gives for the potential of the mercury-mercuric iodate couple,

$$2IO_3^- + Hg = Hg(IO_3)_2(s) + 2e^-, \qquad E^\circ = -0.40.$$

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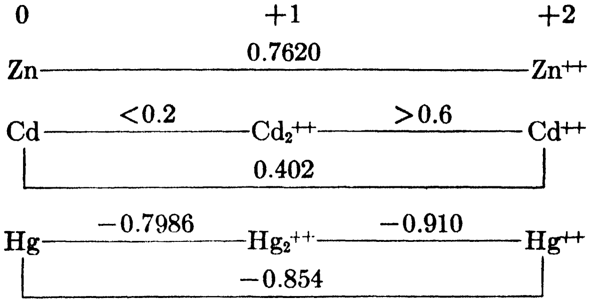
[37] Franklin, E. C., J. Am. Chem. Soc., **29**, 40 (1907).

[38] Drucker, C., *Messungen elektromotorischer Kräfte* (Verlag Chemie, Berlin, 1929), p. 213.

Summary of the Subgroup II potentials. For comparisons within the group, the potentials relating the metals with the ions in acid solution are summarized in the following scheme:



The change from the electropositive character of zinc to the noble metal character of mercury is to be noted. The other important relation is the increasing stability of the +1 state with respect to its decomposition into the +2 state and the metal.

CHAPTER XI

Copper, Silver, and Gold

The elements of subgroup I have one *s* electron in the valence level but the group of 10 *d* electrons which has just been filled in the outer shell of the kernel is still fairly unstable. For this reason it is possible to remove one or two electrons from this group in addition to the one *s* electron. Hence these elements form compounds in which the oxidation state is +1, +2, or +3, although there is considerable variation in the relative stabilities of these various states with the different elements.

Copper

The standard state of the element is the solid metal. There is a decided lack of agreement among various investigators as to the heat and free energy of sublimation of copper to form the monatomic gas. However, we shall use the heat given by Bichowsky and Rossini, 81,200 cal.; and this, with the entropy of sublimation, 31.8 cal. per degree, gives 71,700 cal. for the free energy of formation of Cu(g). Randall, Nielsen, and West[1] presented evidence indicating that the vapor contains an appreciable partial pressure of Cu_2 at the boiling point.

Oxidation states. Copper forms compounds of the +1 state, cuprous, and the +2 state, cupric. The existence of the +3 oxidation state is shown by the formation of salts of the acid oxide, Cu_2O_3, but it and the +3 ion are such powerful oxidizing agents that they are very unstable in water solution.

The copper-cuprous couple. Fenwick[2] has made a careful study of the equilibrium between copper, and cupric and cuprous ions and computes,

$$Cu = Cu^+ + e^-, \qquad E° = -0.522$$

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[1] Randall, M., Nielsen, R. F., and West, G. H., Ind. Eng. Chem., **23**, 388 (1931).

[2] Fenwick, F., J. Am. Chem. Soc., **48**, 860 (1926)

The corresponding free energy of cuprous ion is 12,040 cal. She gives for the equilibrium

$$Cu + Cu^{++} = 2Cu^{+}, \qquad K = 1.0 \times 10^{-6}.$$

However, in the presence of ions or molecules which form very stable complex ions with cuprous, this equilibrium is shifted far to the right.

The copper-cuprous oxide couple. The data on the free energy of cuprous oxide have been summarized by Randall, Nielsen, and West.[3] They chose −34,990 cal. from a study of nine different determinations. Taking into account our different value for the free energy of water and other auxiliary data which enter into the calculations, we shall take −35,150 cal. for the Cu_2O free energy. Hence,

$$2OH^{-} + 2Cu = Cu_2O + H_2O + 2e^{-}, \qquad E^{\circ} = 0.361.$$

The corresponding solubility product of cuprous oxide is

$$\tfrac{1}{2}Cu_2O + \tfrac{1}{2}H_2O = Cu^{+} + OH^{-}, \qquad K = 1.2 \times 10^{-15}.$$

The copper-cuprous halide couples. Nielsen and Brown[4] measured the potential of the Cu—CuCl couple against hydrogen and the CuCl—Cu^{++} couple against chlorine. From the former, one computes −28,345 cal. and from the latter −28,718 cal. for the free energy of cuprous chloride. Watanabe[5] calculates from equilibrium measurements −28,490 cal.; and, since this value is a good mean of the other values, it will be adopted.

$$Cl^{-} + Cu = CuCl + e^{-}, \qquad E^{\circ} = -0.124$$

$$CuCl = Cu^{+} + Cl^{-}, \qquad K = 1.85 \times 10^{-7}$$

For the free energies of cuprous bromide and iodide, Ishikawa, Yamazaki, and Murooka[6] report −23,812 and −16,658 cal., respectively. Small corrections for the auxiliary data employed in their calculations should be made, but since they are probably within the experimental errors, these values will be used.

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[3] Randall, M., Nielsen, R. F., and West, G. H., Ind. Eng. Chem., **23**, 388 (1931).

[4] Nielsen, R. F., and Brown, D. J., J. Am. Chem. Soc., **50**, 9 (1928).

[5] Watanabe, M., Science Rep. Tohoku Imp. Univ., **23**, 115 (1934).

[6] Ishikawa, F., Yamazaki, S., and Murooka, T., Science Rep. Tohoku Imp. Univ., **23**, 115 (1934).

$$\mathrm{Br}^- + \mathrm{Cu} = \mathrm{CuBr} + e^-, \qquad E^\circ = -0.033$$

$$\mathrm{CuBr} = \mathrm{Cu}^+ + \mathrm{Br}^-, \qquad K = 5.3 \times 10^{-9}$$

$$\mathrm{I}^- + \mathrm{Cu} = \mathrm{CuI} + e^-, \qquad E^\circ = 0.187$$

$$\mathrm{CuI} = \mathrm{Cu}^+ + \mathrm{I}^-, \qquad K = 1.1 \times 10^{-12}$$

Noyes and Chow[7] reported,

$$\mathrm{CuCl} + \mathrm{Cl}^- = \mathrm{CuCl_2}^-, \qquad K = 6.5 \times 10^{-2}.$$

Using our value for the solubility product,

$$\mathrm{CuCl_2}^- = \mathrm{Cu}^+ + 2\mathrm{Cl}^-, \qquad K = 2.9 \times 10^{-6}.$$

From the work of Bodländer and Storbeck[8]

$$\mathrm{CuBr} + \mathrm{Br}^- = \mathrm{CuBr_2}^-, \qquad K = 4.6 \times 10^{-3}$$

$$\mathrm{CuI} + \mathrm{I}^- = \mathrm{CuI_2}^-, \qquad K = 7.8 \times 10^{-4}$$

and again combining with our values for the solubility products,

$$\mathrm{CuBr_2}^- = \mathrm{Cu}^+ + 2\mathrm{Br}^-, \qquad K = 1.2 \times 10^{-6}$$

$$\mathrm{CuI_2}^- = \mathrm{Cu}^+ + 2\mathrm{I}^-, \qquad K = 1.4 \times 10^{-9}.$$

The corresponding free energies are: $\mathrm{CuCl_2}^-$, −58,300 cal.; $\mathrm{CuBr_2}^-$, −45,000 cal.; and $\mathrm{CuI_2}^-$, −24,600 cal.; but high accuracy cannot be claimed for these values. The potentials of the copper-cuprous complex ion couples are:

$$2\mathrm{Cl}^- + \mathrm{Cu} = \mathrm{CuCl_2}^- + e^-, \qquad E^\circ = -0.19$$

$$2\mathrm{Br}^- + \mathrm{Cu} = \mathrm{CuBr_2}^- + e^-, \qquad E^\circ = -0.05$$

$$2\mathrm{I}^- + \mathrm{Cu} = \mathrm{CuI_2}^- + e^-, \qquad E^\circ = 0.00$$

Because of this complex ion formation, these E° values and not the E° values for the solid salts are significant in solutions containing the halide ion in excess.

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[7] Noyes, A. A., and Chow, M., J. Am. Chem. Soc., **40**, 739 (1918).

[8] Bodländer, G., and Storbeck, O., Z. anorg. Chem., **31**, 458 (1902).

The copper-cuprous cyanide and thiocyanate couples. There appears to be no reliable data on the potentials of cuprous cyanide and thiocyanate. The following values are estimated from the work of Spitzer[9] on cuprous cyanide and of Immerwahr[10] on cuprous thiocyanate:

$$Cu(CN)_2^- = Cu^+ + 2CN^-, \qquad K = 1 \times 10^{-16}$$

$$CuCNS = Cu^+ + CNS^-, \qquad K = 4 \times 10^{-14}$$

The approximate potentials are:

$$2CN^- + Cu = Cu(CN)_2^- + e^-, \qquad E^\circ = \text{ca } 0.43$$

$$CNS^- + Cu = CuCNS + e^-, \qquad E^\circ = \text{ca } 0.27$$

No value of the constant for the complex thiocyanate ion can be given.

Copper-cuprous sulfide and other cuprous couples. From the Bichowsky and Rossini heat of formation, $-18{,}970$ cal., and the entropy of formation, 5.3 cal. per degree, the free energy of formation of cuprous sulfide (α form), is found to be $-20{,}550$ cal. Randall, Nielsen, and West[11] give $-19{,}955$, and we shall use $-20{,}200$.

$$S^{--} + 2Cu = Cu_2S + 2e^-, \qquad E^\circ_B = 0.95$$

The cuprous sulfide is stable with respect to its decomposition into copper and cupric sulfide,

$$Cu_2S = CuS + Cu, \qquad \Delta F^\circ = 8445 \text{ cal.}$$

However, cupric sulfide is stable with respect to its decomposition into sulfur and cuprous sulfide,

$$2CuS = Cu_2S + S, \qquad \Delta F^\circ = 3310 \text{ cal.}$$

For the solubility product of cuprous sulfide one calculates

$$Cu_2S = 2Cu^+ + S^{--}, \qquad K = 2.5 \times 10^{-50}$$

The cuprous ion forms complexes with thiosulfate, probably $Cu(S_2O_3)_2^{---}$, but data are not available for the evaluation of this free energy.

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[9] Spitzer, F., Z. Elektrochem., **11**, 345 (1905).

[10] Immerwahr, C., Z. anorg. Chem., **24**, 269 (1900).

[11] Randall, M., Nielsen, R. F., and West, G. H., Ind. Eng. Chem., **23**, 388 (1931).

Bjerrum[12] has made an extensive study of cuprous and cupric ammonia complex ions. His work was at 18° C., and one cannot convert his results to 25° with accuracy. Bjerrum gave,

$$Cu(NH_3)_2^+ = Cu(NH_3)^+ + NH_3, \qquad K = 1.16 \times 10^{-5}$$

$$Cu(NH_3)_2^+ = Cu^+ + 2NH_3, \qquad K = 1.35 \times 10^{-11}$$

He found 0.1080 for the $E°$ potential of the Cu—$Cu(NH_3)_2^+$ couple. We shall write,

$$2NH_3 + Cu = Cu(NH_3)_2^+ + e^-, \qquad E° = 0.11$$

The copper-cupric ion couple. Lewis and Randall[13] give for the potential of the copper-cupric ion couple

$$Cu = Cu^{++} + 2e^-, \qquad E° = -0.3448,$$

and for the free energy of the ion, 15,910 cal. Reducing agents in acid solution reduce cupric ion to copper unless there is present a substance which forms a very stable compound with cuprous ion, for example, metallic iron precipitates copper from copper sulfate, but iodide ion forms $CuI(s)$ or CuI_2^-.

The copper-cupric oxide or hydroxide couple. For the free energy of cupric oxide, Randall, Nielsen, and West[14] select −30,300 cal. from the results of a number of investigations. Making some allowance for our new values for the free energy of water which enters into many of the calculations, we will take −30,400 cal. These authors calculate from the work of Allmand,

$$Cu_2O + 3H_2O = 2Cu(OH)_2 + H_2, \qquad \Delta F° = 34{,}344 \text{ cal.}$$

This would make the free energy of the hydroxide −85,430 cal. Allmand calculated the solubility product of the hydroxide to be 1.0×10^{-19} which would give −85,168 as the free energy. From the Bichowsky and Rossini heat of formation of the blue solid, −106,700 cal., and the entropy of formation, −69.7 cal. per degree (assuming the entropy of $Cu(OH)_2$ is 18.5), we find the free energy of formation to be −85,900 cal. We shall use −85,500 for this value, and make the following calculations:

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[12] Bjerrum, J., Kgl. Danske Videnskab. Selskab. Math-fys., **12**, No. 15 (1934).

[13] Lewis, G. N., and Randall, M., *Thermodynamics* (McGraw-Hill, New York, 1923), p. 433.

[14] Randall, M., Nielsen, R. F., and West, G. H., Ind. Eng. Chem., **23**, 388 (1931).

$$2OH^- + Cu = CuO + H_2O + 2e^-, \qquad E_B^\circ = 0.258$$

$$2OH^- + Cu = Cu(OH)_2 + 2e^-, \qquad E_B^\circ = 0.224$$

$$CuO + H_2O = Cu(OH)_2, \qquad \Delta F^\circ = 1590$$

$$Cu(OH)_2 = Cu^{++} + 2OH^-, \qquad K = 5.6 \times 10^{-20}$$

$$Cu_2O = CuO + Cu, \qquad \Delta F^\circ = 4750$$

From the last equation it appears that cuprous oxide is stable with respect to its decomposition into cupric oxide and copper.

McDowell and Johnston[15] have given the following constants for cupric oxide in alkaline solutions:

$$CuO + OH^- = HCuO_2^-, \qquad K = 1.03 \times 10^{-5}$$

$$CuO + 2OH^- = CuO_2^{--} + H_2O, \qquad K = 8.1 \times 10^{-5}$$

$$HCuO_2^- = H^+ + CuO_2^{--}, \qquad K = 7.9 \times 10^{-14}$$

The corresponding free energies of formation are $HCuO_2^-$, −61,325 cal. and CuO_2^{--}, −43,310 cal. For the solubility of the hydroxide in alkali we compute,

$$Cu(OH)_2 + 2OH^- = 2H_2O + CuO_2^{--}, \qquad K = 1.2 \times 10^{-3}$$

The copper-cupric sulfide couple. Randall, Nielsen, and West calculate from the third law that the free energy of cupric sulfide is −11,557 cal. and we shall use their value.

$$S^{--} + Cu = CuS + 2e^-, \qquad E_B^\circ = 0.76$$

$$CuS = Cu^{++} + S + 2e^-, \qquad E^\circ = -0.60$$

$$CuS = Cu^{++} + S^{--}, \qquad K = 4 \times 10^{-38}$$

Other copper-cupric couples. Haehnel[16] reports, at 18° C.,

$$CuCO_3 = Cu^{++} + CO_3^{--}, \qquad K = 1.37 \times 10^{-10}$$

From this the free energy of copper carbonate is −123,930 cal. and

$$CO_3^{--} + Cu = CuCO_3 + 2e^-, \qquad E_B^\circ = -0.053.$$

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[15] McDowell, L. A., and Johnston, H. L., J. Am. Chem. Soc., **58**, 2009 (1936).

[16] Haehnel, O., J. prakt. Chem., **108**, 189 (1924).

The concentration of cupric ion in equilibrium with the various basic carbonates is certainly very much less than that for the normal carbonate.

The solubility product of copper iodate appears to be 1.3×10^{-7}, from the work of Spencer,[17] by e.m.f. measurements in which the concentrations and not the activities were used to evaluate the constant.

Jellinek and Gordon[18] give the concentration of Cu^{++} in equilibrium with the complex tartrate ion (10^{-3} *M*) and 1*M* OH^- as 10^{-15}. They write

$$\frac{(Cu^{++})^2\,(Tart.)^2}{(Complex)\,(H^+)^4} = K,$$

but there appears to be some uncertainty regarding the formula of the complex ion.

For the dissociation constants of the cupric ammonia complex ions, Bjerrum[19] reports, at 18° C.,

$$Cu(NH_3)_5^{++} = Cu(NH_3)_4^{++} + NH_3, \qquad K = 2.8$$

$$Cu(NH_3)_4^{++} = Cu^{++} + 4NH_3, \qquad K = 4.56 \times 10^{-14}.$$

As an approximation for 25° we shall write,

$$4NH_3 + Cu = Cu(NH_3)_4^{++} + 2e^-, \qquad E^\circ = 0.05.$$

Various cuprous-cupric couples. From the data given above one may calculate the potentials of many couples relating copper in the +1 and +2 oxidation states.

$$Cu^+ = Cu^{++} + e^-, \qquad E^\circ = -0.167$$

$$H_2O + 2OH^- + Cu_2O = 2Cu(OH)_2 + 2e^-, \qquad E_B^\circ = 0.087$$

$$CuCl = Cu^{++} + Cl^- + e^-, \qquad E^\circ = -0.566$$

$$CuBr = Cu^{++} + Br^- + e^-, \qquad E^\circ = -0.657$$

$$CuI = Cu^{++} + I^- + e^-, \qquad E^\circ = -0.877$$

$$CuI_2^- = Cu^{++} + 2I^- + e^-, \qquad E^\circ = -0.690$$

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[17] Cf. Auerbach, F., Z. physik. Chem., **86**, 243 (1914).

[18] Jellinek, K., and Gordon, H., Z. physik. Chem., **112**, 207 (1924).

[19] Bjerrum, J., Kgl. Danske Videnskab. Selskab. Math-fys., **12**, No. 15 (1934).

$$Cu(CN)_2^- = Cu^{++} + 2CN^- + e^-, \qquad E_B^\circ = \text{ca } -1.12$$

$$CuCNS = Cu^{++} + 2CNS^- + e^-, \qquad E_B^\circ = \text{ca } -0.96$$

$$2NH_3 + Cu(NH_3)_2^+ = Cu(NH_3)_4^{++} + e^-, \quad E_B^\circ = 0.0$$

$$S^{--} + Cu_2S = 2CuS + 2e^-, \qquad E_B^\circ = 0.58$$

It follows from these potentials that, in each of the couples given in this list except the first one, cupric copper will be reduced to the cuprous state and not to copper by the addition of a small amount of a suitable reducing agent.

Copper in the +3 state. Hypochlorite in alkaline solution dissolves cupric hydroxide apparently with the formation of CuO_2^-. The sesquioxide has not been prepared, but the slightly soluble calcium salt may be precipitated. In acid solution. oxygen is rapidly evolved. From these facts,

$$Cu(OH)_2 = CuO_2^- + H_2O + e^-, \qquad E_B^\circ < -0.8$$

$$Cu^{++} = Cu^{+++} + e^-, \qquad E^\circ < -1.8$$

Silver

The standard state of the element is the solid metal. Van Liempt[20] has reviewed the data on the vapor pressure of silver. From the heat of sublimation, 68,000 cal., and the entropy of sublimation, 31.1 cal. per degree, the free energy of sublimation is found to be 58,700 cal.

The oxidation states of silver. Although the ions of +2 and +3 silver are known, they are such powerful oxidizing agents that they are unstable in water solutions with respect to their reduction by the water. The +1 silver ion forms many slightly soluble compounds and slightly ionized complex ions. For most of these, data are available for the evaluation of their free energies.

The silver-silver ion couple. The value of Lewis and Randall for the silver-silver ion couple will be used.

$$Ag = Ag^+ + e^-, \qquad E^\circ = -0.7995$$

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[20] Van Liempt, J. A. M., Z. anorg. allgem. Chem., **114**, 105 (1920).

The free energy of formation of silver ion then is 18,441 cal. The couple is capable of attaining rapid reversible equilibrium, and makes an excellent electrode for e.m.f. measurements. Silver is readily precipitated by cathodic reduction and the silver coulometer is one of the most accurate instruments for the measurement of the quantity of electricity flowing in a circuit.

The silver-silver oxide couple. Pitzer and Smith[21] have determined the entropy of silver oxide and summarized the data pertaining to its free energy of formation. From their work, this value will be taken to be −2590 cal.

$$2OH^- + 2Ag = Ag_2O + H_2O + 2e^-, \qquad E_B^\circ = -0.344$$

$$\tfrac{1}{2}Ag_2O + \tfrac{1}{2}H_2O = Ag^+ + OH^-, \qquad K = 2.0 \times 10^{-8}$$

The silver halide and cyanide couples. The following calculations are based on the work of Randall and Young,[22] Randall and Halford,[23] and Harned and Ehlers:[24]

$$Cl^- + Ag = AgCl + e^-, \qquad E^\circ = -0.2222$$

$$AgCl = Ag^+ + Cl^-, \qquad K = 1.7 \times 10^{-10}$$

$$Br^- + Ag = AgBr + e^-, \qquad E^\circ = -0.073$$

$$AgBr = Ag^+ + Br^-, \qquad K = 3.3 \times 10^{-13}$$

$$I^- + Ag = AgI(ppt.) + e^-, \qquad E^\circ = 0.151$$

$$AgI(ppt.) = Ag^+ + I^-, \qquad K = 8.5 \times 10^{-173}$$

$$AgI(ppt.) = AgI(hexag.), \qquad \Delta F^\circ = -531 \text{ cal.}$$

$$CN^- + Ag = AgCN + e^-, \qquad E_B^\circ = 0.04$$

$$AgCN = Ag^+ + CN^-, \qquad K = 7.0 \times 10^{-15}$$

$$2CN^- + Ag = Ag(CN)_2^- + e^-, \qquad E_B^\circ = 0.29$$

$$Ag(CN)_2^- = Ag^+ + 2CN^-, \qquad K = 3.8 \times 10^{-19}$$

$$CNS^- + Ag = AgCNS + e^-, \qquad E_B^\circ = -0.09$$

$$AgCNS = Ag^+ + CNS^-, \qquad K = 1.0 \times 10^{-12}$$

[21] Pitzer, K. S., and Smith, W. V., J. Am. Chem. Soc., **59**, 2633 (1938).

[22] Randall, M., and Young, L. E., J. Am. Chem. Soc., **50**, 989 (1928).

[23] Randall, M., and Halford, J O., J. Am. Chem. Soc., **52**, 178 (1930).

[24] Harned, H. S., and Ehlers, R. W., J. Am. Chem. Soc., **55**, 2179 (1933).

The corresponding free energies of formation are: AgCl, −26,220 cal.; AgBr, −22,900 cal.; AgI(ppt.), −15,810 cal.; AgCN, 38,500 cal.; and $Ag(CN)_2^-$, 72,050 cal. Silver ion also forms complex ions with excess bromide, iodide, and thiocyanate; but Randall and Halford conclude that there are a number of types of complex ions present and that it is at present impossible to calculate the various equilibrium constants (cf. Bodländer and Fittig[25] who gave −0.12 for the $Ag—Ag(CNS)_4^{---}$ couple).

The complex silver ammonia, sulfite, and thiosulfate ions. From the calculations of Randall[23] the dissociation constants and potentials of the following complex ions may be given:

$$\begin{aligned}
Ag(NH_3)_2^+ &= Ag^+ + 2NH_3(aq), & K &= 6.0 \times 10^{-8} \\
2NH_3(aq) + Ag &= Ag(NH_3)_2^+ + e^-, & E^\circ &= -0.373 \\
Ag(S_2O_3)_2^{---} &= Ag^+ + 2S_2O_3^{--}, & K &= 4.2 \times 10^{-14} \\
2S_2O_3^{--} + Ag &= Ag(S_2O_3)_2^{---} + e^-, & E^\circ &= -0.01 \\
Ag(SO_3)_2^{---} &= Ag^+ + 2SO_3^{--}, & K &= 3.0 \times 10^{-9} \\
2SO_3^{--} + Ag &= Ag(SO_3)_2^{---} + e^-, & E^\circ &= -0.30
\end{aligned}$$

For the free energies of the ions one computes: $Ag(NH_3)_2^+$, −4060 cal.; $Ag(S_2O_3)_2^{---}$, −248,000 cal.; and $Ag(SO_3)_2^{---}$, −226,000 cal.

The silver-silver sulfide couple. Noyes and Freed[27] measured the equilibrium between silver iodide and silver sulfide. From their value for this reaction we calculate −9425 cal. for the free energy of formation of silver sulfide. They also made e.m.f. measurements upon the silver–silver sulfide electrode and these results led to −9558 cal. Kimura[28] reports −9542. The third-law value, using the Bichowsky and Rossini heat of formation, is −7600 cal. but this would become −9000 if Thomsen's determination of the heat were used. We shall select −9500 cal.

$$\begin{aligned}
S^{--} + 2Ag &= Ag_2S + 2e^-, & E^\circ &= 0.71 \\
Ag_2S &= 2Ag^+ + S^{--}, & K &= 1.0 \times 10^{-51} \\
Ag_2S &= 2Ag^+ + S + 2e^-, & E^\circ &= -1.04
\end{aligned}$$

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[25] Bodländer, G., and Fittig, R., Z. physik. Chem., **39**, 597 (1902).
[26] Cf. Randall, M., International Critical Tables, **VII**, 267.
[27] Noyes, A. A., and Freed, E. S., J. Am. Chem. Soc., **42**, 476 (1920).
[28] Kimura, G., Bull. Inst. Phys. Chem. Res. Tokyo, **13**, 464 (1934).

Additional silver-silver salt potentials. From the tabulation by Randall[29] we may write:

$$AgNO_2 = Ag^+ + NO_2^-, \qquad K = 2.4 \times 10^{-4}$$

$$NO_2^- + Ag = AgNO_2 + e^-, \qquad E^\circ = -0.59$$

$$\Delta F^\circ(\text{formation})\ AgNO_2 = 4960 \text{ cal.}$$

$$AgBrO_3 = Ag^+ + BrO_3^-, \qquad K = 5.20 \times 10^{-5}$$

$$BrO_3^- + Ag = AgBrO_3 + e^-, \qquad E^\circ = -0.55$$

$$AgIO_3 = Ag^+ + IO_3^-, \qquad K = 5.3 \times 10^{-8}$$

$$IO_3^- + Ag = AgIO_3 + e^-, \qquad E^\circ = -0.37$$

$$\Delta F^\circ(\text{formation})\ AgIO_3 = -24{,}080 \text{ cal.}$$

Walker, Bray, and Johnston[30] studied the silver-silver carbonate electrode. From their work

$$Ag_2CO_3 = 2Ag^+ + CO_3^{--}, \qquad K = 8.2 \times 10^{-12}$$

$$CO_3^{--} + 2Ag = Ag_2CO_3 + 2e^-, \qquad E_B^\circ = -0.47$$

$$\Delta F^\circ(\text{formation})\ Ag_2CO_3 = -104{,}600 \text{ cal.}$$

From the Hass and Jellinek[31] value for the solubility product of silver oxalate,

$$Ag_2C_2O_4 = 2Ag^+ + C_2O_4^{--}, \qquad K = 1.1 \times 10^{-11}$$

$$C_2O_4^{--} + 2Ag = Ag_2C_2O_4 + 2e^-, \qquad E^\circ = -0.47$$

The following values for silver cyanate are from the data by Birckenbach and Huttner:[32]

$$AgCNO = Ag^+ + CNO^-, \qquad K = 2.3 \times 10^{-7}$$

$$CNO^- + Ag = AgCNO + e^-, \qquad E^\circ = -0.41$$

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[29] Cf. Randall, M., International Critical Tables, **VII**, 271.

[30] Walker, A. C., Bray, U. B., and Johnston, J., J. Am. Chem. Soc., **49**, 1256 (1927).

[31] Hass, K., and Jellinek, K., Z. physik. Chem., **162**, 157 (1932).

[32] Birckenbach, L., and Huttner, K., Z. anorg. allgem. Chem., **190**, 26 (1930).

Cann and Mueller,[33] studied the potential of the Ag—Ag_2CrO_4 couple and reviewed the literature on silver chromate. We shall use their values,

$$CrO_4^{--} + 2Ag = Ag_2CrO_4 + 2e^-, \qquad E^\circ = -0.446$$

$$Ag_2CrO_4 = 2Ag^+ + CrO_4^{--}, \qquad K = 1.1 \times 10^{-12}$$

The following data were given by Pearce and Ough,[34]

$$Fe(CN)_6^{----} + 4Ag = Ag_4Fe(CN)_6 + 4e^-, E^\circ = -0.194$$

$$Ag_4Fe(CN)_6 = 4Ag^+ + Fe(CN)_6^{----},$$

$$K = 1.55 \times 10^{-41}$$

For the Ag—AgN_3 couple, Taylor and Nims[35] reported,

$$HN_3 + Ag = AgN_3 + H^+ + e^-, \qquad E^\circ = -0.292$$

These authors gave the solubility of AgN_3 as 5.1×10^{-5} *M*.

Latimer, Hicks, and Schutz[36] computed 6722 cal. for the free energy of solution of silver sulfate. Hence,

$$Ag_2SO_4 = 2Ag^+ + SO_4^{--}, \qquad K = 1.18 \times 10^{-5}$$

$$SO_4^{--} + 2Ag = Ag_2SO_4 + 2e^-, \qquad E^\circ = -0.653$$

$$\Delta F^\circ(\text{formation})\ Ag_2SO_4 = -145{,}940 \text{ cal.}$$

The values listed below are from the solubility products by Britton and German:[37]

$$Ag_2MoO_4 = 2Ag^+ + MoO_4^{--}, \qquad K = 3.1 \times 10^{-11}$$

$$MoO_4^{--} + 2Ag = Ag_2MoO_4 + 2e^-, \qquad E^\circ = -0.49$$

$$Ag_2WO_4 = 2Ag^+ + WO_4^{--}, \qquad K = 5.2 \times 10^{-10}$$

$$WO_4^{--} + 2Ag = Ag_2WO_4 + 2e^-, \qquad E^\circ = -0.53$$

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[33] Cann, J. Y., and Mueller, G. B., J. Am. Chem. Soc., **57**, 2525 (1935).

[34] Pearce, J. N., and Ough, L. D., J. Am. Chem. Soc., **60**, 80 (1938).

[35] Taylor, A. C., and Nims, L. F., J. Am. Chem. Soc., **60**, 262 (1938).

[36] Latimer, W. M., Hicks, J. F. G., Jr., and Schutz, P. W., J. Chem. Phys., **1**, 424 (1933).

[37] Britton, H. T. S., and German, W. L., J. Chem. Soc., 1159 (1934).

The following values are derived from the tabulation by Drucker:[38]

$$AgC_2H_3O_2 = Ag^+ + C_2H_3O_2^-, \qquad K = 1.9 \times 10^{-3}$$

$$C_2H_3O_2^- + Ag = AgC_2H_3O_2 + e^-, \qquad E^\circ = -0.64$$

Silver in the +2 and +3 oxidation states. Noyes and his coworkers[39] studied the Ag^+—Ag^{++} couple in HNO_3 and $HClO_4$. With acid molalities of 4, they found $E = -1.927$ in HNO_3 and $E = -1.970$ in $HClO_4$. The difference obviously arises from complex nitrate formation. The E° involves the extrapolation to zero ionic strength, which cannot be made at present. We shall write:

$$Ag^+ = Ag^{++} + e^-, \qquad E^\circ = -1.98$$

These investigators, having prepared Ag^{++} solutions by the action of ozone upon Ag^+, present convincing evidence to show that the mechanism of the reaction involved the following steps:

$$Ag^+ + O_3 = AgO^+ + O_2$$

$$AgO^+ + 2H^+ + Ag^+ = 2Ag^{++} + H_2O$$

The last reaction reaches equilibrium with the ratio of Ag^{++}/AgO^+ quite large. Assuming that ΔF° for this second reaction is approximately -5000 cal., one calculates

$$H_2O + Ag^{++} = AgO^+ + 2H^+ + e^-, \qquad E^\circ = \text{ca } -2.1$$

$$H_2O + Ag^+ = AgO^+ + 2H^+ + 2e^-, \qquad E^\circ = \text{ca } -2.0$$

The potential of the Ag^{++}—AgO^+ couple could hardly be much greater negatively than 2.2 and permit the formation of AgO^+ from ozone which has a potential of -2.07. This potential cannot be much less and still keep the ratio of Ag^{++}/AgO^+ high. The Ag^{++} ion appears to be a rapid oxidizing agent, and the catalytic action of silver ion upon the rate of oxidation by peroxysulfate is certainly connected with the formation of these higher oxidation states of silver. In agreement with the potentials the free energy of formation of Ag^{++} is 63,150 cal.

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[38] Drucker, C., *Messungen elektromotorischer Kräfte* (Verlag Chemie, Berlin, 1929), p. 212.

[39] Noyes, A. A., DeVault, D., Coryell, C. D., and Deahl, T. J., J. Am. Chem. Soc., **59**, 1326 (1937). Corrected for new γ value of $HClO_4$ by DeVault (unpublished).

Luther and Pokorny[40] measured the potential of AgO and Ag_2O_3 in alkaline solution and their results have been confirmed by a number of workers (cf. Jirsa and Jelinek[41]).

$$2OH^- + Ag_2O = 2AgO + H_2O + 2e^-, \qquad E^\circ_B = -0.57$$

$$2OH^- + 2AgO = Ag_2O_3 + H_2O + 2e^-, \qquad E^\circ_B = -0.74$$

The corresponding free energies of formation are: AgO, 2600 cal., and Ag_2O_3, 10,500 cal. However, it has not been definitely established that the Ag_2O_3 in the cell measurements is a pure substance.

TABLE 27

E° VALUES FOR COMPOUNDS OF Ag^+ IN ORDER OF DECREASING CONCENTRATIONS OF Ag^+

Substance	E°	Substance	E°
Ag^+	−0.7995	$AgIO_3$	−0.37
$AgC_2H_3O_2$	−0.64	Ag_2O	−0.344
Ag_2SO_4	−0.65	$Ag(SO_3)_2^{---}$	−0.30
$AgNO_2$	−0.59	AgCl	−0.222
Ag_2BrO_3	−0.55	$Ag_4Fe(CN)_6$	−0.19
Ag_2WO_4	−0.53	AgCNS	−0.09
Ag_2MoO_4	−0.49	AgBr	−0.073
Ag_2CO_3	−0.47	$Ag(S_2O_3)_2^{---}$	−0.01
$Ag_2C_2O_4$	−0.47	AgCN	0.04
Ag_2CrO_4	−0.45	AgI	0.150
AgCNO	−0.41	$Ag(CN)_2^-$	0.29
$Ag(NH_3)_2^+$	−0.37	Ag_2S	0.71

For convenience in comparing the stability of the silver compounds, the E° values for the metal to +1 silver have been summarized in Table 27. For the slightly soluble compounds the order is that of decreasing solubility in a one molal solution of the ion, but for two salts of the types Ag_2X and AgY this is not necessarily the order of their solubilities in pure water because of the $(Ag^+)^2$ factor in the first type.

Gold

The standard state of the element is the solid metal. Ruff and Bergdahl[42] have reviewed the data on the vapor pressure at high temperatures. From the Bichowsky and Rossini heat of sublimation, 92 kcal., and the entropy of sublimation, 31.7 cal. per degree, the free energy of sublimation is found to be 82.5 kcal.

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[40] Luther, R., and Pokorny, F., Z. anorg. Chem., **57**, 291 (1908).

[41] Jirsa, F., and Jelinek, J., Z. anorg. allgem. Chem., **158**, 61 (1926).

[42] Ruff, O., and Bergdahl, B., Z. anorg. allgem. Chem., **106**, 76 (1919).

Oxidation states. Auric ion, Au^{+++}, is the only simple ion which is stable in water solutions at appreciable concentrations. However, a number of complex ions of the aurous state, Au^+, exist and the very insoluble +2 sulfide, AuS, is stable; but all other compounds of this state are decomposed by water.

Gold-auric couples. The free energy of formation of auric oxide appears to be accurately established. The investigations both of Gerke and Rourke[43] and of Buehrer and Roseveare[44] are in accord and give

$$3H_2 + Au_2O_3 = 2Au + 3H_2O, \qquad E^\circ = 1.363$$

The free energy of the oxide then is 18,710 cal.

These e.m.f. measurements were made in acid solution and Jirsa and Jelinek[45] have measured the solubility of the hydroxide in nitric acid. Since both the oxide and hydroxide are fairly soluble in acid, it seems most probable that the solid phase $Au_2O_3 \cdot nH_2O$ at equilibrium was the same in both investigations. The reported solubility was 3×10^{-5} moles of gold in 0.45 molal nitric acid at 21° C. Using 0.73 as the activity coefficient of the acid,

$$\tfrac{1}{2}Au_2O_3 + \tfrac{3}{2}H_2O = Au^{+++} + 3OH^-, \qquad K = 8.5 \times 10^{-45}$$

One then computes for the Au—Au^{+++} couple,

$$Au = Au^{+++} + 3e^-, \qquad E^\circ = -1.42$$

The corresponding free energy of the ion is 98,200 cal.

The oxide is quite soluble in OH^- to form aurate, AuO_2^-, but there are no data on the free energy of this reaction. From a rough approximation of the solubility we estimate,

$$4OH^- + Au = AuO_2^- + 2H_2O + 3e^-, \qquad E_B^\circ = \text{ca } -0.5$$

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[43] Gerke, R. H., and Rourke, M. D., J. Am. Chem. Soc., **49**, 1855 (1927).

[44] Buehrer, T. F., and Roseveare, W. E., J. Am. Chem. Soc., **49**, 1989 (1927).

[45] Jirsa, F., and Jelinek, J. Z. Elektrochem., **30**, 286 and 535 (1924).

Bjerrum and Kirschner[46] have measured the potential of the gold-auric complex chloride couple at 18° C.

$$4Cl^- + Au = AuCl_4^- + 3e^-, \qquad E^\circ = -1.00$$

$$AuCl_4^- = Au^{+++} + 4Cl^-, \qquad K = 5 \times 10^{-22}$$

$$\Delta F^\circ(\text{formation})\ AuCl_4^- = -56{,}200 \text{ cal.}$$

For the potential of the corresponding bromide complex, Grube and Morita[47] report, at 60° C.,

$$4Br^- + Au = AuBr_4^- + 3e^-, \qquad E^\circ = -0.87$$

The value at 25° C. probably does not differ by more than 0.02 volts.

Iodide reduces $AuCl_4^-$ to AuI and the cyanide complex ion $Au(CN)_4^-$ is unstable upon warming with respect to $Au(CN)_2^-$ and cyanogen. Bjerrum and Kirschner give the K for $Au(CNS)_4^-$ as 3×10^{-38}.

The gold-aurous couples. Aurous ion is unstable with respect to its decomposition into gold and auric ion and the ratio Au^+/Au^{+++} is so small that no accurate measurement has been made of the concentration of aurous ion in any solution. For this reason no direct experimental value can be given for the Au—Au^+ couple. However we may make some calculations which will give us an approximate figure for the potential.

The heat of formation of aurous iodide as given by Fischer and Biltz,[48] 200 cal., is in excellent accord with the older value by Thomsen of 300 cal. The entropy of aurous iodide is not known but a value of 28.5 cal. per degree given by the equation of Latimer[49] is probably accurate to at least one entropy unit. Hence ΔS° of formation is 3.2 and ΔF°, −760 cal.

$$I^- + Au = AuI + e^-, \qquad E^\circ = -0.50$$

The error in this potential is probably not more than 0.02 volts. A knowledge of the solubility product of aurous iodide would permit a calculation of the Au—Au^+ couple. The solubility products for CuI and AgI are about 10^{-12} and 10^{-16}, respectively, and an extrapolation of these values together with the general trend of halide solubilities in this region of the periodic system would place the solubility product of AuI about 10^{-20}. The use of this figure would give

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[46] Bjerrum, N., and Kirschner, A., Kgl. Danske Videnskab. Selskab. Math-fys., V, No. 1 (1918).

[47] Grube, G., and Morita, T., Z. Elektrochem., **38**, 117 (1932).

[48] Fischer, W., and Biltz, W., Z. anorg. allgem. Chem., **176**, 81 (1928).

[49] Latimer, W. M., J. Am. Chem. Soc., **43**, 818 (1921).

$$\begin{aligned} Au &= Au^{+} + e^{-}, & E^{\circ} &= \text{ca } -1.68 \\ Au^{+} &= Au^{+++} + 2e^{-}, & E^{\circ} &= \text{ca } -1.29 \\ 3Au^{+} &= Au^{+++} + 2Au, & K &= \text{ca } 1 \times 10^{13} \end{aligned}$$

ΔF°(formation) Au^{+} = ca 38,700 cal.

Aurous oxide, Au_2O, is sufficiently soluble so that it is unstable, in contact with water, with respect to the decomposition into the metal and Au_2O_3.

Bodländer[50] gave

$$2CN^{-} + Au = Au(CN)_2^{-} + e^{-}, \qquad E^{\circ} = 0.60$$

This potential is remarkably high and leads to a value of the dissociation constant of the complex ion,

$$Au(CN)_2^{-} = Au^{+} + 2CN^{-}, \qquad K = \text{ca } 5 \times 10^{-39}$$

As indicated by the potential, gold, in the presence of cyanide, is a powerful reducing agent and is very readily oxidized by oxygen. This reaction is the basis of the cyanide process for the extraction of gold from low grade ores.

Bjerrum and Kirschner[51] have studied the thiocyanate complex ions $Au(CNS)_2^{-}$ and $Au(CNS)_4^{-}$. At 18° C. they found

$$\begin{aligned} 2CNS^{-} + Au &= Au(CNS)_2^{-} + e^{-}, & E^{\circ} &= -0.69 \\ 2CNS^{-} + Au(CNS)_2^{-} &= Au(CNS)_4^{-} + 2e^{-}, & E^{\circ} &= -0.645 \end{aligned}$$

From these potentials it is obvious that $Au(CNS)_2^{-}$ is unstable,

$$3Au(CNS)_2^{-} = 2Au + Au(CNS)_4^{-} + 2CNS^{-}, \qquad K = 33$$

However, they also found,

$$Au(CNS)_4^{-} = Au(CNS)_2^{-} + (CNS)_2, \qquad K = 0.49 \times 10^{-4}$$

Grube and Morita[52] gave for 60° C.

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[50] Bodländer, G., Ber., **36**, 3933 (1903).

[51] Bjerrum, N., and Kirschner, A., Kgl. Danske Videnskab. Selskab Math-fys., V, No. 1 (1918).

[52] Grube, G., and Morita, T., Z. Elektrochem., **38**, 117 (1932).

$$2\text{Br}^- + \text{Au} = \text{AuBr}_2^- + e^-, \qquad E^\circ = -0.96$$

and combining with their potential for Au—AuBr_4^-

$$2\text{Br}^- + \text{AuBr}_2^- = \text{AuBr}_4^- + 2e^-, \qquad E^\circ = -0.82.$$

It follows that AuBr_2^- is unstable with respect to the decomposition into Au and AuBr_4^-.

Claims are made for the formation of aurous sulfide, Au_2S, and also the thio acid ion, AuS^-, but nothing is known regarding their free energies.

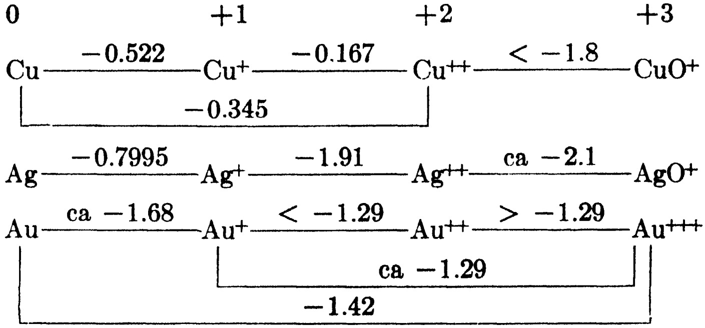
Gold in the +2 oxidation state A number of compounds of +2 gold have been prepared, as for example AuCl_2, at high temperatures, but the only one stable in contact with water appears to be the sulfide. This is doubtless because of its very slight solubility, for although the solubility product is unknown, one would judge from mercuric sulfide that it must be very small. The sulfide is formed by the action of hydrogen sulfide upon auric chloride and is soluble in polysulfide to form thioaurates, but no energy values can be given for those reactions. From our approximate value for the Au^+—Au^{+++} couple and the knowledge that Au^{++} must oxidize and reduce itself to give Au^+ and Au^{+++}, one can set the limits,

$$\text{Au}^{++} = \text{Au}^{+++} + e^-, \qquad E^\circ > -1.29$$

$$\text{Au}^{+} = \text{Au}^{++} + e^-, \qquad E^\circ < -1.29$$

but no estimate can be given of the concentration of Au^{++} present in the Au^+—Au^{+++} equilibrium.

Summary of Subgroup I potentials. For comparison, the potentials relating the oxidation states of the three elements of the group are summarized in the following scheme:



CHAPTER XII

Nickel, Palladium, and Platinum

Each element of this group marks the end of a so-called "transition series" in which 10 *d* electrons have been added to the preceding noble gas. However, the groups of *d* electrons are not yet fully stabilized, and even in the monatomic gas molecules, the d^9s^1 state has just about the same energy as the d^{10} state, that is, one of the electrons may be present in the next higher *s* level. Because of this instability, a number of electrons may be removed by chemical oxidation; hence the group has oxidation numbers ranging at least as high as +6. The more important oxidation states are +2 and +4, but there is considerable variation in the relative stabilities of the various states with the different elements.

Nickel

The standard state of the element is the solid metal. Kelley[1] gave the free energy of sublimation as 87,433 cal.

Oxidation states. The +1 cyanide, NiCN, exists, and possibly so do some other unstable compounds of this state. The +2 state is by far the most important and in water solution the chemistry of nickel is very largely that of the ion, Ni^{++}, and its compounds. Although the oxide, Ni_2O_3, may be prepared, it probably is not a true +3 compound, but a mixture of the +2 and +4 oxides. No other compounds of the +3 state exist. The +4 oxide, NiO_2, is a very powerful oxidizing agent, and compounds of the +4 state are not known in acid solution. There is some evidence of +6 and +8 oxides.

The nickel-nickelous couple. An accurate value for the potential of the Ni—Ni^{++} couple cannot be given, as a truly reversible equilibrium appears to be practically unattainable. Colombier[2] gave −0.227. Haring and Vanden Bosche[3] report

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[1] Kelley, K. K., U. S. Bur. Mines Bull., 383 (1935).

[2] Colombier, L., Compt. rend., **199**, 273 (1934).

[3] Haring, M. M., and Vanden Bosche, E. G., J. Phys. Chem., **33**, 161 (1929).

-0.231. Murata[4] found -0.248. Using the Bichowsky and Rossini heat of formation of Ni^{++}, $-15{,}200$ cal., and assuming that the entropy of Ni^{++} is -26 cal. per degree, the same as Fe^{++} and Cu^{++}, the potential would be -0.316. No great reliance can be placed in the heat of formation, and the entropy of the ion may differ from the ferrous and cupric values by several units because of the different multiplicity of the ground state. See also Co--Co^{++} potential. We shall write

$$Ni = Ni^{++} + 2e^-, \qquad E^\circ = 0.250.$$

The corresponding free energy of formation of Ni^{++} is $-11{,}530$ cal.

The nickel-nickel hydroxide couple. We shall use the solubility product of nickel hydroxide to calculate the potential of the nickel couple in alkaline solution. Britton[5] reported 8.7×10^{-19} for K, but this is certainly too small. Wijs[6] gave 1.6×10^{-14} from a study of the equilibrium with the ammonia complex ion. The third-law value is in agreement, if we correct the Bichowsky and Rossini heats of formation, to bring the heat of formation of Ni^{++} into agreement with our free energy of this ion. Hence

$$Ni(OH)_2 = Ni^{++} + 2OH^-, \qquad K = 1.6 \times 10^{-14}$$

$$2OH^- + Ni = Ni(OH)_2 + 2e^-, \qquad E^\circ_B = 0.66.$$

Based on this potential the free energy of formation of $Ni(OH)_2$ is $-105{,}600$ cal.

Complex nickelous ions. Wijs[7] reports

$$Ni(NH_3)_4^{++} = Ni^{++} + 4NH_3(aq), \qquad K = 4.8 \times 10^{-8}$$

$$Ni(NH_3)_6^{++} = Ni^{++} + 6NH_3(aq), \qquad K = 2.1 \times 10^{-8}$$

Hence

$$6NH_3(aq) + Ni = Ni(NH_3)_6^{++} + 2e^-, \qquad E^\circ = 0.48$$

Nickelous ion forms a complex with cyanide, $Ni(CN)_4^{--}$. From the heat of the reaction, 44 kcal., we estimate very roughly the K to be 10^{-22}, but entropy values used in the computation may be badly in error.

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[4] Murata, K., Bull. Chem. Soc. Japan, **3**, 57 (1928).
[5] Britton, H. T. S., J. Chem. Soc., **127**, 2110 (1925).
[6] Wijs, H. J. de, Rec. trav. chim., **44**, 663 (1925).
[7] *Ibid.*

Powerful reducing agents reduce $Ni(CN)_4^{--}$ to the +1 complex ion $Ni(CN)_3^{--}$. Grube[8] has measured the potential,

$$CN^- + Ni(CN)_3^{--} = Ni(CN)_4^{--} + e^-, \qquad E^\circ = 0.82$$

Nickel carbonate and sulfide. For the solubility product of the carbonate, Ageno and Valla[9] reported,

$$NiCO_3 = Ni^{++} + CO_3^{--}, \qquad K = 1.36 \times 10^{-7}$$

From this value one computes,

$$CO_3^{--} + Ni = NiCO_3 + 2e^-, \qquad E^\circ = 0.45.$$

Taking the heat of precipitation of the sulfide, NiS, as −15,080 cal., and the ΔS° the same as for FeS, 47.5 cal. per degree, the solubility product is 3×10^{-22}. Theil and Gessner[10] conclude that there are three forms of nickel sulfide with the solubility products: α, 3×10^{-21}; β, 1×10^{-26}; γ, 2×10^{-28}. The α form, mixed with some β and γ, is precipitated in cold alkaline solution. This would agree with the solubility calculated above from the heat of precipitation of nickel with sodium sulfide. The conversion of α nickel sulfide to the other forms is favored by acid, which explains the well-known fact that nickel and cobalt sulfides do not dissolve in hydrochloric acid but cannot be precipitated from acid solution by hydrogen sulfide. Based on the Theil and Gessner constants,

$$S^{--} + Ni = NiS(\alpha) + 2e^-, \qquad E^\circ = 0.86$$

$$S^{--} + Ni = NiS(\gamma) + 2e^-, \qquad E^\circ = 1.07$$

Nickelic oxide. The oxidation of nickelous hydroxide in alkaline solution appears to form either a solid solution or a series of compounds of NiO_2 and NiO with some water of hydration. With fairly high concentrations of hydroxide, it is probably possible to obtain pure NiO_2.[11] This oxide mixture is the oxidizing agent used in the Edison storage battery, and the electrode is often considered as the $Ni(OH)_2$—$Ni(OH)_3$ couple. Foerster[12] has studied the potential of the electrode, and from his work we shall write

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[8] Grube, G., Z. Elektrochem., **32**, 561 (1926).

[9] Ageno, F., and Valla, E., Atti. Accad. Lincei, Ser. 5, **20:2**, 706 (1911).

[10] Theil, A., and Gessner, H., Z. anorg. Chem., **86**, 49 (1914).

[11] Cf. Howell, O. R., J. Chem. Soc., **123**, 1772 (1923).

[12] Foerster, F., Z. Elektrochem., **13**, 414 (1907).

$$2OH^- + Ni(OH)_2 = NiO_2 + 2H_2O + 2e^-, \qquad E^\circ_B = -0.49.$$

The couple is readily reversible as is indicated by its use in the nickel accumulator. For the Ni^{++}—NiO_2 couple in acid, we compute,

$$2H_2O + Ni^{++} = NiO_2 + 4H^+ + 2e^-, \qquad E^\circ = -1.75.$$

This potential is sufficient to cause the rapid oxidation of water, so the oxide is unstable in acid solutions.

Higher oxidation states of nickel. When nickelous hydroxide is fused with potassium nitrate and potassium hydroxide, the nickelate compound, K_2NiO_4, is formed. It also is unstable in acid solutions because of its high oxidizing power.

$$4H_2O + Ni^{++} = NiO_4^{--} + 8H^+ + 4e^-, \qquad E^\circ < -1.8$$

Claims are also made for the formation by the same process of some pernickelate, K_2NiO_5, but the evidence is not conclusive.

Palladium

The standard state of the element is the metal. The entropy of sublimation, 31.3 cal. per degree, is not too well known and the heat of sublimation, 110 kcal., by Bichowsky and Rossini is only a rough estimate. The corresponding free energy of sublimation is 101 kcal.

The element absorbs hydrogen to a remarkable extent, 600 to 900 volumes of the gas per volume of the metal, depending upon its physical condition. The hydrogen appears to be present as a solid solution of the compound, Pd_2H. Gillespie and Hall[13] report for 30° C.,

$$Pd_2H(\text{in sat. Pd}) = 2Pd(\text{in sat. }Pd_2H) + \tfrac{1}{2}H_2, \quad P = 0.0246\,\text{atm.}$$

The solution is a very much more rapid reducing agent than hydrogen (cf. hydrogen overvoltage) and, for example, reduces ferric ion readily.

Oxidation states. The most important oxidation state is the +2. Claims are made for the existence of some +1 compounds but they cannot be considered as substantiated. The

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[13] Gillespie, L. J., and Hall, F. P., J. Am. Chem. Soc., **48**, 1207 (1926).

+4 oxidation state is represented by the dioxide and complex chlorides, for example, K_2PdCl_6, and there is evidence of the +6 oxide, PdO_3.

Palladium-palladous couples. Neumann[14] measured the potential of palladium in 0.5 *M* $PdCl_2$ against the calomel electrode and found −0.79 for the couple. He also found in a similar cell Cd—$CdCl_2$(aq), 0.442. Making the correction on the palladium couple, which is necessary to give the correct $E°$ value for the cadmium couple, one obtains,

$$Pd = Pd^{++} + 2e^-, \qquad E° = -0.83$$

This value is in agreement with the chemical facts that palladium dissolves slowly in nitric acid and is precipitated from a nitrate solution by ferrous ion. The corresponding free energy of formation of Pd^{++} is 38,300 cal.

The data on the couple in alkaline solution are somewhat puzzling. The heat of formation of the oxide, PdO, has been obtained from its decomposition pressures, and the heat of formation of the hydroxide, $Pd(OH)_2$, may be calculated from the heat of precipitation. By making estimates on the entropy of formation, which cannot be greatly in error, one obtains as $E°$ values for the couples, Pd—PdO, −0.1 and for Pd—$Pd(OH)_2$, −0.1. Jirsa[15] reported for Pd—Pd_2O, −0.15 and for Pd_2O—PdO, −0.4 to −0.5. These values were obtained by anodic oxidation and it is possible that the first one is spurious, perhaps resulting from oxidation of some Pd_2H in the electrode. On the other hand, this −0.15 value is in approximate agreement with that calculated from thermal data for the Pd—PdO couple. In view of the low solubility of platinous hydroxide we shall adopt the lower value and write

$$2OH^- + Pd = Pd(OH)_2 + 2e^-, \qquad E°_B = -0.1$$

$$Pd(OH)_2 = Pd^{++} + 2OH^-, \qquad K = \text{ca } 1 \times 10^{-24}$$

The heat of formation of the complex chloride is given by Bichowsky and Rossini as −127,500 cal. Estimating the entropy of the ion as 40 cal. per degree, the free energy of formation is −96,000 cal. and

$$4Cl^- + Pd = PdCl_4^{--} + 2e^-, \qquad E° = -0.64.$$

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[14] Neumann, B., Z. physik. Chem., **14**, 193 (1894).

[15] Jirsa, F., Z. physik. Chem., **113**, 241 (1924).

This seems to be about right, as ferrous ion will not precipitate the metal from the complex chloride. The corresponding dissociation constant is,

$$PdCl_4^{--} = Pd^{++} + 4Cl^-, \qquad K = \text{ca}\ 3 \times 10^{-7}.$$

The thermal data on the complex bromide appear to give a slightly larger constant for its dissociation and are probably in error.

No values can be given for the dissociation constant of the complex ammonia ion or for the solubility product of the slightly soluble salts, $Pd(CN)_2$, $PdI_2 \cdot H_2O$, and PdS.

Palladium in the +4 and +6 oxidation states. Wellman[16] found by direct measurement,

$$PdCl_4^{--} + 2Cl^- = PdCl_6^{--} + 2e^-, \qquad E° = -1.288$$

The recorded heats of formation are not in agreement with this potential and it would appear that the heat of formation of $PdCl_6^{--}$ should be about −145,000 cal. instead of −156,500 cal. The complex chloride is almost as good an oxidizing agent as chlorine, and chlorine is evolved from the solution upon heating. Wellman also measured the solubility product of the potassium salt.

$$K_2PdCl_6(s) = 2K^+ + PdCl_6^{--}, \qquad K = 6.0 \times 10^{-6}$$

The complex bromide may be prepared but it also is unstable upon warming with respect to the oxidation of bromide. The concentration of Pd^{+4}, or some hydrolyzed form of the ion, in these solutions is unknown but it is probably less than 10^{-10}.

$$Pd^{++} = Pd^{+4} + 2e^-, \qquad E° < -1.6$$

Jirsa[17] gave −0.95 for the PdO—PdO_2 couple in alkali. From the thermal data we calculate −0.71 for $Pd(OH)_2$—$Pd(OH)_4$. As an approximation we shall write,

$$2OH^- + Pd(OH)_2 = Pd(OH)_4 + 2e^-, \qquad E°_B = \text{ca}\ -0.8.$$

The same author reported,

$$2OH^- + PdO_2 = PdO_3 + H_2O + 2e^-, \quad E°_B = -1.2.$$

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[16] Wellman, H. B., J. Am. Chem. Soc., **52**, 985 (1930).
[17] Jirsa, F., Z. physik. Chem., **113**, 241 (1924).

The trioxide in acid solution is obviously a very powerful oxidizing agent and no compounds are known.

Platinum

The standard state of the element is the solid metal. Jones, Langmuir, and Mackay[18] calculate the boiling point as 4800° K. and the vapor pressure at 1000° K. as 3.47×10^{-9} atm. Their value for the heat of sublimation is $\Delta H_{0^\circ K.} = 127{,}500$ cal. Kelley[19] calculated $\Delta F^\circ = 114{,}900$ cal.

Oxidation states. The principal oxidation states are the +2 and +4. The free ions corresponding to these states are present only at low concentrations in water solutions but many halogeno-, nitro-, amido-, cyano-, and other complex platinites and platinates exist in solution. These compounds are, in general, much more stable and important than the oxides and their complexes. However, the free energy data pertaining to the platinum complex acids are very limited and only a few cases can be discussed. The +1 and +3 chlorides and a few other compounds of these states have been prepared, but their chemistry has no significance in water solutions. The +6 oxide and a few salts, for example, K_2PtO_4, are known.

Platinum-platinous couples. Many investigators have been discouraged by the lack of reproducibility of platinum electrodes. Lorenz and Spielmann[20] discuss the problem for a number of couples. However, although their potentials were not very constant, they do agree in general with values which we may calculate from thermal data. For the hydroxide, $Pt(OH)_2$, Bichowsky and Rossini give −87,500 cal. as the heat of formation. Estimating the entropy of the hydroxide as 24.5, one computes for the entropy of formation −65.7 cal. per degree and for the free energy, −67,900 cal. Hence

$$2OH^- + Pt = Pt(OH)_2 + 2e^-, \qquad E_B^\circ = -0.16$$

The hydroxide is not appreciably soluble in 1 molal acid; hence we may write,

$$2H_2O + Pt = Pt(OH)_2 + 2H^+ + 2e^-, \qquad E^\circ = -0.99$$

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[18] Jones, H. A., Langmuir, I., and Mackay, G. M. J., Phys. Rev., **30**, 201 (1927).

[19] Kelley, K. K., U. S. Bur. Mines Bull., 383 (1935).

[20] Lorenz, R., and Spielmann, P. E., Z. Elktrochem., **15**, 293 (1909).

Lorenz and Spielmann found -0.98 as an average of a number of values for this couple.

However, the hydroxide dissolves somewhat in concentrated nitric acid, and, as a rough estimate, the solubility product is

$$Pt(OH)_2 = Pt^{++} + 2OH^-, \qquad K = \text{ca } 10^{-35}.$$

This leads to the following potential for the ion:

$$Pt = Pt^{++} + 2e^-, \qquad E^\circ = \text{ca } -1.2$$

Using $-122{,}000$ cal. as the heat of formation of the chloroplatinite, $PtCl_4^{--}$, and estimating the entropy of the ion as 45, the entropy of formation is -102.8 cal. per degree and the free energy, $-91{,}600$ cal. From this value,

$$4Cl^- + Pt = PtCl_4^{--} + 2e^-, \qquad E^\circ = -0.73$$

$$PtCl_4^{--} = Pt^{++} + 4Cl^-, \qquad K = \text{ca } 10^{-16}$$

A similar calculation for the bromoplatinite yields,

$$4Br^- + Pt = PtBr_4^{--} + 2e^-, \qquad E^\circ = -0.68$$

$$PtBr_4^{--} = Pt^{++} + 4Br^-, \qquad K = \text{ca } 10^{-18}$$

Lorenz and Spielmann found -0.726 for the Pt—$PtCl_4^{--}$ couple. This value is consistent with the fact that ferric chloride slowly oxidizes platinum, but may be a little too large negatively.

The heat of formation of platinous sulfide, PtS, is given by Bichowsky and Rossini as $-16{,}000$ cal. Taking the entropy of the sulfide equal to that of lead sulfide, 21.8, the entropy of formation is 4.2 cal. per degree and the free energy, $-17{,}250$ cal.

$$H_2S(g) + Pt = PtS + 2H^+ + 2e^-, \qquad E^\circ = 0.20$$

$$S^{--} + Pt = PtS + 2e^-, \qquad E^\circ_B = 0.83$$

$$PtS = Pt^{++} + S^{--}, \qquad K = \text{ca } 10^{-70}$$

According to these potentials, platinum should tarnish with hydrogen sulfide. However, the energy of the reaction is not very large.

$$H_2S + Pt = PtS + H_2, \qquad \Delta F^\circ = -9400 \text{ cal.}$$

It is obvious that the solubility product of PtS must be very small in order for it to be stable, but the figure 10^{-70} seems a little excessive, although it must be said that it is very difficult to put PtS into solution by oxidation of the sulfur. However, a value of −12,000 cal. for the heat of formation of the sulfide would appear to be more reasonable.

Free energies cannot be calculated for the numerous ammonia and nitrite complex salts. The iodoplatinite is unstable,

$$2PtI_4^{--} = PtI_6^{--} + 2I^- + Pt$$

Platinum in the +3 state. From the heats of formation, the heat of the decomposition of the trichloride is found to be

$$2PtCl_3(s) = PtCl_2(s) + PtCl_4(s), \quad \Delta H^\circ = \Delta F^\circ = 3.4 \text{ kcal.}$$

The entropy of the reaction must be very small; hence ΔH° and ΔF° are approximately the same. This small positive value indicates that the solid is stable. Experimentally it also dissolves in water without decomposition, but when it is warmed with hydrochloric acid the following reaction occurs,

$$2PtCl_3 + 4Cl^- = PtCl_4^{--} + PtCl_6^{--}$$

and there appears to be no appreciable concentration of +3 platinum complex ions in the solution.

Platinous-platinic couples. The potential of the $PtCl_4^{--}$—$PtCl_6^{--}$ couple has been measured by a number of investigators. Smith[21] gave −0.792 for the couple in 0.1 N Cl^- and we shall write

$$2Cl^- + PtCl_4^{--} = PtCl_6^{--} + 2e^-, \qquad E^\circ = -0.72.$$

The heat of the similar reaction (that is, with H_2—$2H^+$) for the bromoplatinites and platinates is 4100 cal. less, and assuming the entropy of the two reactions to be closely the same, one calculates,

$$2Br^- + PtBr_4^{--} = PtBr_6^{--} + 2e^-, \qquad E^\circ = -0.63.$$

No data are available for the calculation of the dissociation constants of the chloro- or bromoplatinates. The acid dissociation constants of many of nitro-, chloro-, and amido-complex ions have been studied by Grünberg and Faermann.[22] For example, they give,

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[21] Smith, E R., U. S. Bur. Standards J. Research, **5**, 735 (1930).

[22] Grünberg, A. A., and Faermann, G. P., Z. anorg. allgem. Chem., **193**, 193 (1930).

$$Pt(NH_3)_6^{+4} = Pt(NH_3)_5(NH_2)^{+++} + H^+, \quad K = 1.3 \times 10^{-9}$$

However we cannot at present calculate free energies for these complex ions.

Terrey[23] gave the following value for the cyanide couple in chloride solution:

$$2Cl^- + Pt(CN)_4^{--} = PtCl_2(CN)_4^{--} + 2e^-, \qquad E^\circ = -0.89$$

From the solubility data, rough values may be obtained by the solubility products of many of the chloroplatinates, for example,

$$K_2PtCl_6 = 2K^+ + PtCl_6^{--}, \qquad K = 1 \times 10^{-5}$$

$$(NH_4)_2PtCl_6 = 2NH_4^+ + PtCl_6^{--}, \qquad K = 9 \times 10^{-6}$$

The silver salt is but very slightly soluble.

The heats of formation of the dioxide, PtO_2, or the platinic acid, $H_2Pt(OH)_6$, have not been determined. Platinous hydroxide is readily oxidized in air to the dioxide or, in alkaline solution, to platinate.

$$4OH^- + Pt(OH)_2 = Pt(OH)_6^{--} + 2e^-, \quad E_B^\circ = -0.1 \text{ to } -0.4$$

Since platinum hydroxide does not decompose in acid into the metal and the dioxide, the potential of the $Pt(OH)_2$—PtO_2 couple must be less than that for the Pt—$Pt(OH)_2$ couple, that is, < -0.99. Lorenz and Spielmann found -1.01, and we shall write,

$$Pt(OH)_2 = PtO_2 + 2H^+ + 2e^-, \; E^\circ = \text{ca } -1.1$$

The dioxide is soluble in concentrated sulfuric acid, apparently forming the ions $Pt(OH)_2^{++}$ or $Pt(OH)^+$. No values can be given for their free energies.

The heat of formation of the disulfide, PtS_2, is given by Bichowsky and Rossini as $-21,000$ cal. A value of 25.5 is probably fairly close for the entropy of the sulfide, so the entropy of formation is approximately zero and the free energy of formation is also $-21,000$ cal. With this value we may calculate

$$H_2S(g) + PtS = PtS_2 + 2H^+ + 2e^-, \qquad E^\circ = -0.01$$

$$S^{--} + PtS = PtS_2 + 2e^-, \qquad E_B^\circ = 0.64.$$

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[23] Terrey, H., J. Chem. Soc., 202 (1928).

Since the free energy of the ion Pt^{+4} is not known, we cannot calculate the solubility product. The sulfide is soluble in excess sulfide to form the thioplatinate PtS_3^{--}, but no quantitative figures can be given.

Perplatinate. The anodic oxidation of a solution of platinate in potassium hydroxide results in the deposition of the potassium perplatinate, K_2PtO_4. The oxide, PtO_3, may be prepared from this compound. Since oxygen is not able to bring about this oxidation, one may conclude,

$$2OH^- + Pt(OH)_6^{--} = PtO_4^{--} + 4H_2O + 2e^-, \quad E_B^\circ < -0.4$$

Summary of the group potentials. For comparison of the potentials of the three members of the group, the following summary is given:

ACID SOLUTION

0		+2		+4		+6
Ni	0.250	Ni^{++}	−1.75	NiO_2	< −1.8	NiO_4^{--}
Pd	−0.83	Pd^{++}	< −1.6	Pd^{+4}		
Pt	ca −1.2	Pt^{++}				
	−0.99	$Pt(OH)_2$	ca −1.1	PtO_2		

ALKALINE SOLUTION

Ni	0.66	$Ni(OH)_2$	−0.49	NiO_2	< −0.4	NiO_4^{--}
Pd	−0.1	$Pd(OH)_2$	ca −0.8	$Pd(OH)_4$	ca −1.2	PdO_3
Pt	−0.16	$Pt(OH)_2$	ca −0.2	$Pt(OH)_6^{--}$	< −0.4	PtO_4^{--}

CHAPTER XIII

Cobalt, Rhodium, and Iridium

Each element of this group has nine electrons more than the preceding noble gas. In the monatomic gas atoms the lowest electronic states are s^1d^8 and s^2d^7, the two levels lying close together. The important oxidation states are +2, +3, +4, and +6; the lower states become less stable and the higher states more stable with increasing atomic weight, but compounds of the +6 state are always very powerful oxidizing agents.

Cobalt

The standard state of the element is the solid metal. The only vapor pressure measurements are those of Ruff and Keilig,[1] who gave 30 mm at 2375° K. Millar[2] estimated 85 kcal. as the heat of sublimation. The entropy of the gas has not been calculated, but using 36 cal. per degree for ΔS° of sublimation as an approximation, a rough value for the free energy of sublimation is 74 kcal.

Oxidation states. Like the neighboring elements of the first transition series, cobalt forms compounds of the +2 ion. Unlike nickel but like iron, compounds of the +3 ion exist in solution. The ion, Co^{+++}, is such a powerful oxidizing agent that it decomposes water, but many of its complex ions are more stable than the corresponding cobaltous complex ions. There are, indeed, hundreds of these complex cobaltic ions, and the description of their properties constitutes some of the most interesting pages in chemical literature. The coördination number of +3 cobalt is 6, and ions or molecules in the coördination position are held with remarkable firmness. For example, chloride in such a position is not precipitated by silver ion. However, quantitative data are to be found for only a few ions, and our discussion will be confined to these cases.

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[1] Ruff, O., and Keilig, F., Z. anorg. Chem., **88**, 410 (1914).

[2] Millar, R., Ind. Eng. Chem., **17**, 34 (1925).

There is evidence for the +4 oxide, CoO_2, but the oxide is very unstable in water and the chemistry of this state is therefore limited.

Cobalt-cobaltous couples. Like the nickel electrode, it appears to be impossible to obtain a satisfactory reversible cobalt-cobaltous potential. The following $E°$ values have been calculated from the work of a number of investigators: 0.253, Neumann;[3] 0.298, Labendzenski;[4] 0.292, Coffetti and Foerster;[5] 0.283, Schildbach;[6] 0.246, Lamb and Larson;[7] and 0.278, Haring and Westfall.[8] In addition, Heymann and Jellinek[9] studied the equilibrium between cobalt and nickel and their ions and report $Ni^{++}/Co^{++} = 0.125$. This leads to a difference of 0.027 volts between the $E°$ values of the two elements; and, having chosen 0.250 for nickel, we shall take

$$Co = Co^{++} + 2e^-, \qquad E° = 0.277.$$

This value is a fairly good average of the various e.m.f. measurements. Assuming 27 cal. per degree for the entropy of cobaltous ion and using this potential, one calculates roughly −13,500 cal. for the heat of formation of the ion. This is 3000 cal. less (negatively) than the Bichowsky and Rossini value. All their heats which depend upon the ion will be corrected by this amount when used in later calculations. The free energy of Co^{++} in agreement with the $E°$ is −12,800 cal.

For the solubility product of the hydroxide we compute,

$$Co(OH)_2 = Co^{++} + 2OH^-, \qquad K = 2 \times 10^{-16}.$$

These calculations used −5700 cal. for the heat of precipitation of the hydroxide and an estimated 19 cal. per degree for the entropy of the solid. The calculated free energy of $Co(OH)_2$ is −108,900 cal. and the corresponding potential of the couple in alkaline solution is,

$$2OH^- + Co = Co(OH)_2 + 2e^-, \qquad E°_B = 0.73.$$

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[3] Neumann, B., Z. physik. Chem., **14**, 215 (1894).

[4] Labendzenski, S., Z. Elektrochem., **10**, 77 (1904).

[5] Coffetti, G., and Foerster, F., Ber. **38**, 2936 (1905).

[6] Schildbach, R., Z. Elektrochem., **16**, 967 (1910).

[7] Lamb, A. B., and Larson, A. T., J. Am. Chem. Soc., **42**, 2038 (1920).

[8] Haring, M. M., and Westfall, B. B., Trans. Electrochem. Soc., **65**, 235 (1934).

[9] Heymann, T., and Jellinek, K., Z. physik. Chem., **160**, 34 (1932).

The hydroxide is said to be appreciably soluble in 8 *M* KOH, forming CoO_2^{--}.

Lamb and Larson also studied the cobaltous ammonia complex and found

$$Co(NH_3)_6^{++} = Co^{++} + 6NH_3(aq), \qquad K = 1.25 \times 10^{-5}$$

Combining this with our value for the Co—Co^{++} couple, we find

$$6NH_3(aq) + Co = Co(NH_3)_6^{++} + 2e^-, \qquad E^\circ = 0.422$$

ΔF° (formation) $Co(NH_3)_6^{++} = -57{,}470$ cal.

Cobalt sulfide, like nickel sulfide, has at least two modifications, differing considerably in their solubilities. See, for example, the work of Mickwitz.[10] Taking the entropy of CoS as 16.1, the same as FeS, and using −19,300 cal. as the heat of formation, one computes for the free energy of formation −19,800 cal. Since this heat was obtained by precipitating the sulfide, this calculation should give the value for the more soluble α form. Hence,

$$CoS(\alpha) = Co^{++} + S^{--}, \qquad K = 7 \times 10^{-23}$$

$$S^{--} + Co = CoS(\alpha) + 2e^-, \qquad E_B^\circ = 0.93$$

Kolthoff[11] gave 1.9×10^{-27} for K and this would appear to apply to the less soluble β form. Hence,

$$CoS(\beta) = Co^{++} + S^{--}, \qquad K = 1.9 \times 10^{-27}$$

$$S^{--} + Co = CoS(\beta) + 2e^-, \qquad E_B^\circ = 1.07$$

Kelley and Anderson[12] compute −155,570 cal. for the free energy of formation of cobalt carbonate. Combining with our value for the free energy of cobalt, we find,

$$CoCO_3 = Co^{++} + CO_3^{--}, \qquad K = 1.0 \times 10^{-12}$$

$$CO_3^{--} + Co = CoCO_3 + 2e^-, \qquad E_B^\circ = 0.632$$

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[10] Mickwitz, A., Z. anorg. allgem. Chem., **196**, 116 (1931).

[11] Kolthoff, I. M., J. Phys. Chem., **34**, 2711 (1930).

[12] Kelley, K. K., and Anderson, C. T., U. S. Bur. Mines Bull., 384 (1935).

Cobaltous-cobaltic couples. Noyes and Deahl[13] from potential measurements found in 3*M* HNO_3,

$$Co^{++} = Co^{+++} + e^-, \qquad E = -1.842$$

It is difficult to calculate an accurate $E°$ but we shall use as an approximate value for the free energy of Co^{+++}, 28,900 cal. As this potential indicates, the free ion at high concentrations rapidly oxidizes water to oxygen.

Taking −173,000 cal. for the heat of formation of cobaltic hydroxide and 24 as the estimated entropy of the hydroxide, the entropy of formation is found to be −103.2 cal. per degree, and the free energy to be −142,000 cal.

$$Co(OH)_3 = Co^{+++} + 3OH^-, \qquad K = 2.5 \times 10^{-43}$$

$$OH^- + Co(OH)_2 = Co(OH)_3 + e^-, \qquad E^\circ_B = -0.2$$

Lamb and Larson also studied the dissociation of a number of the cobaltammines. The following constants, which have been calculated from concentrations and not activities, are of special interest:

$$Co(NH_3)_6^{+++} = Co^{+++} + 6NH_3(aq), \qquad K = 2.2 \times 10^{-34}$$

$$Co(NH_3)_5 \cdot H_2O^{+++} = Co^{+++} + 5NH_3(aq) + H_2O,$$
$$K = 1.6 \times 10^{-35}.$$

The aquopentamminecobalti ion is thus slightly more stable than the hexammine. The $Co(NH_3)_5NO_2^{+++}$ and $Co(NH_3)_4(NO_2)_2^{+++}$ ions have stability constants of the same order of magnitude. For the free energies of formation we calculate $Co(NH_3)_6^{+++}$, −55,000 cal. and $Co(NH_3)_5H_2O^{+++}$, −106,000 cal.

$$Co(NH_3)_6^{++} = Co(NH_3)_6^{+++} + e^-, \qquad E° = -0.1.$$

For the potential of the complex cyanide couple, Lieder and Schächterle[14] report 0.814 at 2°C. From this we estimate

$$Co(CN)_6^{-4} = Co(CN)_6^{---} + e^-, \qquad E° = 0.83$$

The cobaltous complex is thus a powerful reducing agent and is even oxidized by water with the evolution of hydrogen.

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[13] Noyes, A. A., and Deahl, T. J., J. Am. Chem. Soc., **59**, 1337 (1937). See also Lamb, A. B., and Larson, A. T., J. Am. Chem. Soc., **42**, 2024 (1920).

[14] Lieder, H., and Schächterle, P., Z. Elektrochem., **32**, 561 (1926).

The potential of the **complex nitrite** couple is not known, but it apparently has a positive $E°$ value and is readily oxidized by HNO_2; hence the cobaltous complex decomposes with the formation of the cobaltic complex and nitric oxide. The solubility of the sodium potassium salt, $NaK_2Co(NO_2)_6 \cdot H_2O$, is given as 0.7 g per liter; hence the solubility product is about

$$NaK_2Co(NO_2)_6 \cdot H_2O = Na^+ + 2K^+ + Co(NO_2)_6^{---} + H_2O,$$

$$K = \text{ca } 2.2 \times 10^{-11}$$

Cobalt dioxide. Powerful oxidizing agents in alkaline solution appear to form the dioxide CoO_2 or a solution of CoO_2 in Co_2O_3. From the curves obtained by Grube[15] for the anodic oxidation of cobalt in hydroxide,

$$OH^- + Co(OH)_3 = CoO_2 + 2H_2O + e^-,$$

the potential at 90° C. would appear to be about -0.7. However, this would lead to a value of -1.5 for the Co^{+++}—CoO_2 couple in acid which is certainly too high by at least 0.3 volts.

Rhodium

The standard state of the element is the solid metal. Bichowsky and Rossini have estimated 115 kcal. as the heat of sublimation, and we estimate 35 as the entropy of sublimation which would give, as a rough approximation, 104,500 cal. as the free energy of sublimation.

Oxidation states. Wöhler and Müller[16] have definitely established the existence of Rh_2O and RhCl, and of RhO and $RhCl_2$. The most important oxidation state is the +3 and, like cobalt, the ion forms many complexes with ammonia, the halogens, cyanide, and nitrite. The dioxide, RhO_2, and trioxide, RhO_3, and their salts in alkaline solution have been prepared but they are too powerful oxidizing agents to exist in acid.

The free energies of some rhodium compounds. Our only source of data regarding the energies of the various oxidation states are a few heats of formation. The calculations leading to the free energies are summarized in Table 28. The entropies have been estimated from the values for similar silver and cadmium compounds. The heats of formation of Bichowsky and Rossini have been used, inasmuch as they appear to be in better agreement with the chemical facts than are those calculated by Wöhler and Jochum.[17]

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[15] Grube, G., Z. Elektrochem., **33**, 394 (1927).

[16] Wöhler, L., and Müller, W., Z. anorg. allgem. Chem., **149**, 125 (1925).

TABLE 28

HEAT ENTROPIES AND FREE ENERGIES OF FORMATION OF RHODIUM COMPOUNDS

Compound	S (Compound)	$\Delta S°$	$\Delta H°$	$\Delta F°$
Rh_2O	(28)	−12	−21,000	−17,400
RhO	(13)	−19	−25,000	−19,300
Rh_2O_3	(30)	−59	−78,000	−60,500
$RhCl$	(23)	−11	−16,000	−12,600
$RhCl_2$	(32)	−29	−40,000	−31,400
$RhCl_3$	(41)	−47	−60,000	−46,000
$RhCl_6^{---}$	(50)	−165	−205,500	−156,000

From these free energies some interesting deductions can be made regarding the stabilities of the +1, +2, and +3 oxidation states. In this connection the following reactions and their free energies are important:

$$3Rh_2O = Rh_2O_3 + 4Rh, \qquad \Delta F° = -8000 \text{ cal.}$$

$$3RhO = Rh_2O_3 + Rh, \qquad \Delta F° = -2600 \text{ cal.}$$

$$3RhCl = RhCl_3 + 2Rh, \qquad \Delta F° = -8200 \text{ cal.}$$

$$3RhCl_2 = 2RhCl_3 + Rh, \qquad \Delta F° = 2200 \text{ cal.}$$

$$3RhCl_2 + 6Cl^- = 2RhCl_6^{---} + Rh, \qquad \Delta F° = -30{,}000 \text{ cal.}$$

Without some knowledge regarding the free energies of solution of the oxides it is impossible to give accurate potentials for the ions. As a rough estimate we shall write,

$$Rh = Rh^{++} + 2e^-, \qquad E° = \text{ca } -0.6$$

$$Rh = Rh^{+++} + 3e^-, \qquad E° = \text{ca } -0.7$$

The metal dissolves in hot concentrated sulfuric acid, which seems reasonable in view of these potentials, but it is not soluble in nitric acid which must mean that the metal is rendered passive with this reagent. The potential for the Rh—Rh^{+++} couple would make the dissociation constant for $RhCl_6^{---}$ about 10^{-12}. This seems to be the right order of magnitude.

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[17] Wöhler, L., and Jochum, N., Z. physik. Chem., **167**, 169 (1933).

No values can be given for the many complex ammines formed by Rh^{+++} or for the sulfide, Rh_2S_3, and the thio-acid. The compound $K_3Rh(NO_2)_6$ has a very small solubility, but there are no quantitative data.

Rhodium in the +4 and +6 states. Chlorine in alkaline solution oxidizes Rh_2O_3 to RhO_2 and forms some RhO_4^{--} in solution. The dioxide has acid properties and forms salts when fused with NaOH. Both RhO_2 and RhO_4^{--} liberate chlorine when treated with hydrochloric acid.

$$2OH^- + Rh_2O_3 = 2RhO_2 + H_2O + 2e^-, \qquad E_B^\circ > -0.9$$

$$4OH^- + RhO_2 = RhO_4^{--} + 2H_2O + 2e^-, \qquad E_B^\circ > -0.9$$

$$2H_2O + RhCl_6^{---} = RhO_2 + 4H^+ + 6Cl^- + e^-, \qquad E^\circ < -1.4$$

$$4H_2O + RhCl_6^{---} = RhO_4^{--} + 8H^+ + 6Cl^- + 3e^-, \qquad E^\circ < -1.4$$

Grube and Gu[18] have studied the oxidation of +3 rhodium in nitric and perchloric acid solutions. Although the form of the +4 ion is not known, we shall give their potentials and write,

$$H_2O + Rh^{+++} = RhO^{++} + 2H^+ + e^-, \qquad E^\circ = -1.40$$

$$3H_2O + RhO^{++} = RhO_4^{--} + 6H^+ + 2e^-, \qquad E^\circ = -1.46$$

Iridium

The standard state of the element is the metal. Based on the estimated heat of sublimation, 115 kcal., and the estimated entropy of sublimation, 35 cal. per degree, the free energy is 105,000 cal.

Oxidation states. The +1 and +2 chlorides have been prepared by the decomposition of $IrCl_3$ at high temperatures. The +3 and +4 states exist in solution in the form of hundreds of complex ions of the same general nature as the cobalt and rhodium complex ions with the exception that the +4 compounds of iridium are much more stable than are those of the lighter elements of the group. The +6 oxide and its salts in alkaline solution are known, but they cannot exist in acid solution.

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[18] Grube, G., and Gu, B., Z. Elektrochem., **43**, 397 (1937).

The free energy of a number of iridium compounds. In Table 29, calculations leading to the free energy of several iridium compounds have been tabulated. The heats of formation are from Bichowsky and Rossini with the exception of that for the dioxide which is the value given by Wöhler and Jochum.[19] The entropies have been estimated from those of similar compounds.

From the free energies of the chlorides, one calculates:

$$3IrCl = IrCl_3 + 2Ir, \qquad \Delta F^\circ = 4200 \text{ cal.}$$

$$3IrCl_2 = 2IrCl_3 + Ir, \qquad \Delta F^\circ = 3000 \text{ cal.}$$

These values indicate that the +1 and +2 chlorides in the solid state are stable with respect to the decompositions as written. However, in contact with water, the greater solubility of the +3 chloride will doubtless cause the reactions to occur.

TABLE 29

HEAT, ENTROPIES, AND FREE ENERGIES OF FORMATION OF IRIDIUM COMPOUNDS

Compound	S (Compound)	ΔS°	ΔH°	ΔF°
$IrCl$	(24)	−12	−20,500	−16,900
$IrCl_2$	(33)	−29	−40,600	−32,000
$IrCl_3$	(42)	−47	−60,500	−46,500
$IrCl_6^{---}$	(51)	−165	−186,800	−137,800
IrO_2	18	−40	−40,000	−28,000

Using the free energy of the +3 chloride complex ion, one calculates,

$$6Cl^- + Ir = IrCl_6^{---} + 3e^-, \qquad E^\circ = -0.72$$

The metal should then dissolve in Cl_2 water or in aqua regia. Upon gentle heating the sesquioxide decomposes,

$$2Ir_2O_3 = 3IrO_2 + Ir;$$

hence we may assume ΔF° for the reaction to be zero and, from the free energy of IrO_2, calculate −42,000 cal. as the free energy of formation of Ir_2O_3.

$$6OH^- + 2Ir = Ir_2O_3 + 3H_2O + 6e^-, \qquad E_B^\circ = -0.1$$

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[19] Wöhler, L., and Jochum, N., Z. physik. Chem., **167**, 169 (1933).

The hydrated oxide is said to be soluble in excess OH^- with the formation of IrO_2^-, but there seems to be some uncertainty regarding the extent to which this reaction takes place.

As a rough approximation, we shall write

$$Ir = Ir^{+++} + 3e^-, \qquad E^\circ = \text{ca } -1.0.$$

This potential would correspond to a dissociation constant, $K = 10^{-14}$ for $IrCl_6^{---}$, and a solubility product, $K = 10^{-45}$ for the oxide, Ir_2O_3.

The +3 – +4 couples. From the free energies one computes,

$$2OH^- + Ir_2O_3 = 2IrO_2 + H_2O + 2e^-, \qquad E^\circ_B = -0.1.$$

The dioxide is not soluble in hydroxide or hydrogen ions. Using the estimated free energy of Ir^{+++}, one finds as an approximate value,

$$2H_2O + Ir^{+++} = IrO_2 + 4H^+ + e^-, \qquad E^\circ = \text{ca } -0.7.$$

This would make Ir^{+++} slightly unstable with respect to its decomposition into the metal and dioxide, which is not correct, but it is difficult with the present data to give a better value.

Woo[20] studied the potential of the $IrCl_6^{---}$—$IrCl_6^{--}$ couple and gave from direct cell measurements,

$$IrCl_6^{---} = IrCl_6^{--} + e^-, \qquad E^\circ = -1.021.$$

The bromoiridate, $IrBr_6^{--}$, forms when the chloroiridate is treated with bromide ion, but the potential of the bromo-couple has not been determined. A similar statement may be made regarding the iodoiridate. No values can be given for the many complex ammines.

Iridium in the +6 state. When the dioxide is fused with potassium nitrate and potassium hydroxide, the salt, K_2IrO_4, is formed and the reaction of oxygen with the dioxide in alkali is also said to occur.

$$4OH^- + IrO_2 = IrO_4^{--} + 2H_2O + 2e^-, \qquad E^\circ_B > -0.4$$

The iridate oxidizes chloride in acid solution.

Summary of group potentials. For comparison, the potentials relating the various oxdiation states of the three elements of the group in acid solutions are summarized in the following scheme:

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[20] Woo, S. C., J. Am. Chem. Soc., **53**, 469 (1931).

$$\begin{tikzcd}
0 & +2 & +3 & +4 & \\
\mathrm{Co} \arrow[r, dash, "0.277"] & \mathrm{Co}^{++} \arrow[r, dash, "-1.82"] & \mathrm{Co}^{+++} \arrow[r, dash, "< -1.8"] & \mathrm{CoO_2} & \\
\mathrm{Rh} \arrow[r, dash, "\text{ca } -0.6"] \arrow[rr, dash, bend right, "\text{ca } -0.7"'] & \mathrm{Rh}^{++} \arrow[r, dash, "\text{ca } -0.9"] & \mathrm{Rh}^{+++} \arrow[r, dash, "\text{ca } -1.4"] & \mathrm{RhO_2} \arrow[r, dash, "\text{ca } -1.4"] & \mathrm{RhO_4}^{--} \\
\mathrm{Ir} \arrow[r, dash, "< -1.0"] \arrow[rr, dash, bend right, "\text{ca } -1.0"'] & \mathrm{Ir}^{++} \arrow[r, dash, "> -1.0"] & \mathrm{Ir}^{+++} \arrow[r, dash, "\text{ca } -0.7"] & \mathrm{IrO_2} \arrow[r, dash, "< -1.4"] & \mathrm{IrO_4}^{--}
\end{tikzcd}$$

CHAPTER XIV

Iron, Ruthenium, and Osmium

The elements of this group have eight electrons more than the preceding noble gas, and these electrons in the gas atoms have the configuration s^2d^6, although the s^1d^7 state also lies very close. The important oxidation numbers are +2, +3, +4, +6, and +8. The latter state is shown in ruthenium and osmium in the tetroxides, RuO_4 and OsO_4, but the maximum oxidation number of iron is +6.

Iron

The standard state of the element is the α metal. Overstreet[1] has reviewed the vapor pressure data on iron and calculates for the process of sublimation: $\Delta H°$, 96,684 cal.; $\Delta F°$, 85,682 cal.; $\Delta S°$, 43.38 cal. per degree.

Oxidation states. The ions Fe^{++}, ferrous, and Fe^{+++}, ferric, exist in acid solution. These ions form the familiar series of ferrous and ferric salts and, in alkaline solution, the corresponding hydroxides. The perferrite ion, FeO_3^{--}, and the ferrate ion, FeO_4^{--}, of the +4 and +6 states, are known in alkaline solutions, but they rapidly evolve oxygen when acidified. There is evidence for low concentrations of the ferryl ion, FeO^{++}, in ferric solutions. Magnetite, Fe_3O_4, or $FeO \cdot Fe_2O_3$, is important in the high temperature chemistry of iron but is not involved in equilibria in water solutions. Claims are made for the +1 state in the compound $(NO)_2FeSK$, but it is obviously difficult to say how the electrons are divided between the nitrogen, iron, and sulfur.

Iron-ferrous couples. Iron electrodes are readily polarized and, in common with other hard metals, surface strains are usually present which are capable of producing very large variations in potential measurements with different samples of the metal. Richards and Behr[2] were the first to get reproducible results using finely divided iron. Randall and Frandsen[3] gave for the free energy of Fe^{++}, −20,310 cal.

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[1] Overstreet, R., (Master's Thesis, University of California, 1930). Cf. Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).

[2] Richards, T. W., and Behr, G. E., Z. physik. Chem., **58**, 301 (1907).

$$Fe = Fe^{++} + 2e^-, \qquad E° = 0.440.$$

For the couple in alkaline solution, these same authors gave

$$2OH^- + Fe = Fe(OH)_2 + 2e^-, \qquad E°_B = 0.877.$$

The corresponding free energy of $Fe(OH)_2$ is −115,660 cal. From the heat of formation of the hydroxide, −135,900 cal., and the estimated entropy of 19 cal. per degree, one computes the free energy to be −115,700 cal., in agreement with the potential value. The solubility product then is,

$$Fe(OH)_2 = Fe^{++} + 2OH^-, \qquad K = 1.65 \times 10^{-15}.$$

The potential for the oxidation of iron by hydrogen ion is 0.440 volts while the potential for the oxidation by water in alkaline solution is only 0.05 volts. This is doubtless the basis for the more rapid rusting of iron in an acid environment, as the first step of the process appears to involve the reduction of hydrogen. The second step, the formation of ferric oxide, arises from the action of oxygen (cf. Fe^{++}—Fe^{+++} couple).

Kelley and Anderson[4] have reviewed the data on ferrous carbonate and give,

$$FeCO_3 = Fe^{++} + CO_3^{--}, \qquad K = 2.11 \times 10^{-11}.$$

Combining with our values for the free energies of the ions, the free energy of the carbonate is −161,260 cal. and the potential of the iron–ferrous carbonate couple,

$$CO_3^{--} + Fe = FeCO_3 + 2e^-, \qquad E° = 0.755$$

Bruner and Zawadzki[5] gave 3.7×10^{-19} for the solubility product of ferrous sulfide. From the heat of formation, −23,100 cal., and the entropy of formation, 2 cal. per degree, one computes −23,700 cal. for the free energy and a solubility product of 2×10^{-20}. Giving more weight to the former, we shall write,

$$FeS = Fe^{++} + S^{--}, \qquad K = 1 \times 10^{-19}$$

$$S^{--} + Fe = FeS + 2e^- \qquad E° = 1.00$$

$$FeS, \Delta F° \text{ (formation)} = -22{,}900 \text{ cal.}$$

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[3] Randall, M., and Frandsen, M., J. Am. Chem. Soc., **54**, 40, 47 (1932).

[4] Kelley, K. K., and Anderson, C. T., U. S. Bur. Mines Bull., 384 (1935).

[5] Bruner, L., and Zawadzki, J., Z. anorg. Chem., **67**, 454 (1910).

Several values have been reported for the Fe—$Fe(CN)_6^{----}$ couple, but the electrode does not appear to be reproducible. From the heat of formation of the ion and a very rough estimate of 68 cal. per degree for its entropy we calculate,

$$6CN^- + Fe = Fe(CN)_6^{-4} + 2e^-, \qquad E^\circ = \text{ca } 1.5$$

$$Fe(CN)_6^{-4} = Fe^{++} + 6CN^-, \qquad K = \text{ca } 10^{-37}$$

The oxalate complex ion, $Fe(C_2O_4)_2^{----}$, has been studied by Schaper[6] but it is difficult to give a value for its dissociation constant.

Manchot and Haunschild[7] measured the partial pressure of nitric oxide in equilibrium with $FeNO^{++}$ and give, for equal concentrations of the ions,

$$FeNO^{++} = Fe^{++} + NO, \qquad K = 1150 \text{ mm.}$$

Ferrous-ferric couples. The potential of the ferrous-ferric couple has been measured in many cells, but accurate corrections for the hydrolysis of ferric ion and for the activities have not been made in the earlier work. Bray and Hershey[8] reviewed the literature and calculated −0.772 for the E°. Schumb, Sherrill, and Sweetser[9] report −0.770. We shall take

$$Fe^{++} = Fe^{+++} + e^-, \qquad E^\circ = -0.771$$

The free energy of ferric ion then is −2530 cal. One computes from this and the free energy of ferrous ion,

$$Fe = Fe^{+++} + 3e^-, \qquad E^\circ = 0.036$$

This potential has little significance since the mechanism is always through the ferrous state. For the reduction of ferric ion by iron,

$$2Fe^{+++} + Fe = 3Fe^{++}, \qquad \Delta F^\circ = -55{,}870 \text{ cal.,}$$
$$K = 1 \times 10^{41}$$

and the concentration of ferric ion at equilibrium with iron and $1\,M$ Fe^{++} is very small.

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[6] Schaper, C., Z. physik. Chem., **72**, 315 (1910).

[7] Manchot, W., and Haunschild, H., Z. anorg. allgem. Chem., **140**, 22 (1924).

[8] Bray, W. C., and Hershey, A. V., J. Am. Chem. Soc., **56**, 1889 (1934).

[9] Schumb, W. C., Sherrill, M. S., and Sweetser, S. B., J. Am. Chem. Soc., **59**, 2360 (1937).

The heat of formation of ferric hydroxide is given by Bichowsky and Rossini as $-197{,}300$ cal. Estimating the entropy as 23.0, the entropy of formation is -103.9 cal. per degree and the free energy $-166{,}300$ cal. For the solubility product,

$$Fe(OH)_3 = Fe^{+++} + 3OH^-, \qquad K = 4 \times 10^{-38}.$$

This value is in agreement with the calculation of Elder[10] and also closely checks the work of Jellinek and Gordon[11] who reported 1×10^{-38}.

For the potential of the ferrous-ferric couple in alkaline solution, we then find,

$$OH^- + Fe(OH)_2 = Fe(OH)_3 + e^-, \qquad E^\circ_B = 0.56$$

Ferrous hydroxide is thus a very much better reducing agent than ferrous ion. This fact is important in connection with the oxidation of iron by oxygen. From the equation,

$$2Fe^{++} + \tfrac{1}{2}O_2 + 2H^+ = 2Fe^{+++} + H_2O$$

it would appear that high hydrogen ion would favor the oxidation of ferrous ion as the energy of the reaction obviously increases. Experimentally the rate of the reaction decreases and hydrogen ion tends to stabilize ferrous solutions against oxidation. It is generally assumed that this slow rate in acid arises from the initial reduction of the O_2 molecule to hydrogen peroxide, which has a potential of only -0.68 volts and that the equilibrium concentration of hydrogen peroxide does not rapidly oxidize ferrous ion. At low acid the hydrolysis of ferric ion and the slight solubility of ferric hydroxide reduces the potential of the Fe^{++}—Fe^{+++} complex sufficiently so that the reaction with oxygen proceeds rapidly. This explanation is doubtless approximately correct although the actual mechanism may be somewhat more complicated.

Bray and Hershey also determined the following constants:

$$Fe^{+++} + H_2O = Fe(OH)^{++} + H^+, \qquad K = 6.0 \times 10^{-3}$$

$$Fe^{+++} + Cl^- = FeCl^{++}, \qquad K = 20.$$

Ferric hydroxide is quite soluble in concentrated alkali with the formation of ferrite ion, FeO_2^-. In 40 per cent sodium hydroxide, ferrous hydroxide forms some hypoferrite, FeO_2^{--} Grube and Gmelin[12] report in such a solution at 80°,

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[10] Elder, L. W., Trans. Am. Electrochem. Soc., **57**, 383 (1930).

[11] Jellinek, K., and Gordon, H., Z. physik. Chem., **112**, 236 (1924).

$$FeO_2^{--} = FeO_2^{-} + e^{-}, \qquad E = 0.68$$

This value would appear to be consistent with the potential of $Fe(OH)_2$—$Fe(OH)_3$ couple.

The ferrocyanide-ferricyanide couple reaches a rapid reversible equilibrium, and many concordant values have been obtained for cells employing this couple in the form of the potassium salts. However, the potential is a function of the potassium ion concentration and the correction to give an accurate $E°$ value becomes very large. With equal concentrations of the two negative ions, the observed potential is around -0.48. Kolthoff and Tomsicek[13] have made a calculation of the $E°$ value and give,

$$Fe(CN)_6^{----} = Fe(CN)_6^{---} + e^{-}, \qquad E° = -0.36$$

From this potential and our approximate K for ferrocyanide, we find,

$$Fe(CN)_6^{---} = Fe^{+++} + 6CN^{-}, \qquad K = \text{ca } 10^{-44}$$

This value seems reasonable in view of the stability of ferricyanide in alkaline solutions with respect to the formation of ferric hydroxide.

Under conditions in which the above couple had a potential of -0.480, Davidson[14] gave for the potentials of the following couples:

$$Fe(CN)_5(NH_3)^{---} = Fe(CN)_5(NH_3)^{--} + e^{-}, \qquad E = -0.374$$

$$Fe(CN)_5(H_2O)^{---} = Fe(CN)_5(H_2O)^{--} + e^{-}, \qquad E = -0.491$$

$$Fe(CN)_5(NO_2)^{---} = Fe(CN)_5(NO_2)^{--} + e^{-}, \qquad E = -0.516$$

Schaper[15] reported,

$$C_2O_4^{--} + Fe(C_2O_4)_2^{--} = Fe(C_2O_4)_3^{---} + e^{-}, \qquad E° = -0.02.$$

This value represents the order of magnitude of the couple but cannot be considered to be an accurate $E°$ value. Since the dissociation of the $Fe(C_2O_4)_2^{--}$ ion is fairly large, the constant for $Fe(C_2O_4)_3^{---}$ must be around 10^{-10}.

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[12] Grube, G., and Gmelin, H., Z. Elektrochem., **26**, 466 (1920).

[13] Kolthoff, I. M., and Tomsicek, W. J., J. Phys. Chem., **39**, 945 (1935).

[14] Davidson, D., J. Am. Chem. Soc., **50**, 2622 (1928).

[15] Schaper, C., Z. physik. Chem., **72**, 315 (1910).

Ferric ion forms a rather stable complex ion with excess fluoride, FeF_6^{---}. This ion does not oxidize iodide to iodine, so we may estimate,

$$6F^- + Fe^{++} = FeF_6^{---} + e^-, \qquad E^\circ > -0.4$$

For the deep red thiocyanate ferric complex, Golzschmidt[16] has given the following constants:

$$Fe(CNS)_3 = Fe^{+++} + 3CNS^-, \qquad K = 2.6 \times 10^{-6}$$

$$Fe(CNS)_6^{---} = Fe(CNS)_3 + 3CNS^-, \qquad K = 3.1 \times 10^{-4}$$

Ferrous and ferric ions form complexes with orthophenanthroline. Walden, Hammett, and Chapman[17] give

$$Fe(C_{12}H_8N_2)_3^{++} = Fe(C_{12}H_8N_2)_3^{+++} + e^-, \qquad E^\circ = -1.14$$

This couple has been widely used as an indicator in dichromate and ceric sulfate titrations because of the brilliant color change from the red ferrous to the blue ferric complex. For the nitro-derivative of phenanthroline, the E° is -1.25.

Jellinek and Gordon[18] gave,

$$Fe_2S_3 = 2Fe^{+++} + 3S^{--}, \qquad K = 10^{-88}$$

This would make the free energy of formation of ferric sulfide about $-55{,}000$ cal. and leads to the following potential:

$$S^{--} + 2FeS = Fe_2S_3 + 2e^-, \qquad E_B^\circ = 0.7$$

From this value it appears that ferric sulfide should not oxidize sulfide to sulfur in alkaline solution, but the two potentials are quite close.

The same authors studied the complex ferric tartrate and report for the reaction,

$$Fe_2(C_4H_4O_6)_3(aq) = 2Fe^{+++} + 3C_4H_4O_6^{--}$$

that (Fe^{+++}) was 10^{-39} in a solution in which tartrate was 1, ferric tartrate was 10^{-3} and hydrogen ion 10^{-14}.

Iron in the +4 and +6 states. In highly alkaline solutions an ion anode may be oxidized to ferrate, FeO_4^{--}. This ion resembles permanganate in color and in acid solution evolves oxygen very rapidly. Grube and Gmelin[19] studied the FeO_2^-—FeO_4^{--} couple at 80° in 40 per cent sodium hydroxide and gave a value $E = -0.55$. Under these conditions they found no formation of perferrite, FeO_3^{--}. Hypochlorite in alkaline solution appears to be unable to oxidize iron to ferrate; hence we shall write

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[16] Golzschmidt, B. A., Izvest. Ivanovo-Voznesensk. Politekh., **7**, 51 (1928).

[17] Walden, G. H., Hammett, L. P., and Chapman, R. P., J. Am. Chem. Soc., **55**, 2649 (1933).

[18] Jellinek, K., and Gordon, H., Z. physik. Chem., **112**, 241 (1924).

$$4OH^- + FeO_2^- = FeO_4^{--} + 2H_2O + 3e^-, \qquad E_B^\circ < -0.9$$

$$4H_2O + Fe^{+++} = FeO_4^{--} + 8H^+ + 3e^-, \qquad E^\circ < -1.9$$

Under certain limited conditions it is probably possible to form perferrite, and if the free ion is unstable with respect to the decomposition into the +3 and +6 states the FeO_2^-—FeO_3^{--} couple must have a lower potential than the FeO_2^-—FeO_4^{--} couple. Slightly soluble perferrites have been prepared.

Bray and Gorin[20] have discussed the evidence regarding the formation of ferryl ion, FeO^{++}, in ferric solutions by the reaction,

$$2Fe^{+++} + H_2O = Fe^{++} + FeO^{++} + 2H^+.$$

A study of the kinetics of a number of ferric reactions at low acid indicates the existence of this equilibrium, but no quantitative data can be given.

Ruthenium

The standard state of the element is the solid metal. Based on the estimated values for heat of sublimation, 120 kcal., and the entropy of sublimation, 44 cal. per degree, the approximate free energy of the process is 107 kcal.

Oxidation states. The controversy over the +1 state seems definitely to be settled by the work of Crowell and Yost.[21] The blue solution formed by reduction of the +3 complex chloride is Ru^{++} and the lower state does not exist. In acid solutions the important oxidation states are the +3 and +4 which exist in the form of many complex ions. Oxidation of +4 ruthenium by powerful oxidizing agents forms the volatile +8 oxide, RuO_4, with unstable +6 and +7 compounds as intermediates. These latter compounds in the form of RuO_4^{--} and RuO_4^- are much more stable in alkaline solution. In addition to the tetroxide, the oxides, Ru_2O_3 and RuO_2, or their hydroxides, may be precipitated from solution.

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[19] Grube, G., and Gmelin, H., Z. Elektrochem., **26**, 466 (1920).
[20] Bray, W. C., and Gorin, M. H., J. Am. Chem. Soc., **54**, 2124 (1932).
[21] Crowell, W. R., and Yost, D. M., J. Am. Chem. Soc., **50**, 374 (1928).

Ruthenium potentials. The only quantitative data we have for ruthenium are the heats of formation of the trichloride, −63,000 cal., and of the dioxide, −52,500 cal. Estimating the entropy of the former as 41 and the latter as 16, the free energies of formation are: $RuCl_3$, −49,200 cal.; and RuO_2, −40,500 cal. Hence we compute,

$$3Cl^- + Ru = RuCl_3(s) + 3e^-, \qquad E^\circ = -0.65$$

$$2H_2O + Ru = RuO_2(s) + 4H^+ + 4e^-, \qquad E^\circ = -0.79$$

$$4OH^- + Ru = RuO_2(s) + 2H_2O + 4e^-, \qquad E^\circ_B = 0.04.$$

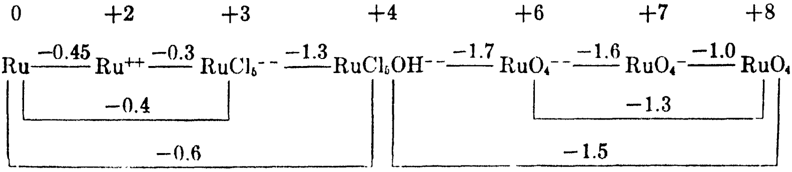
None of these couples have chemical significance, since the solids cannot exist in equilibrium with one molal solutions of the ions. However, they do aid in the estimation of the couples which we wish to write. Thus, in hydrochloric acid, $RuCl_3$ forms $RuCl_5^{--}$, and RuO_2 forms $RuCl_5OH^{--}$. We do not know the free energies of these reactions, but in neither case does the complex ion appear to be unusually stable. As approximate values, the following will be used:

$$5Cl^- + Ru = RuCl_5^{--} + 3e^-, \qquad E^\circ = \text{ca } -0.4$$

$$5Cl^- + H_2O + Ru = RuCl_5OH^{--} + H^+ + 4e^-, \qquad E^\circ = \text{ca } -0.6.$$

In choosing these potentials the following facts were considered: the $RuCl_5^{--}$—$RuCl_5OH^{--}$ potential must be just a little more positive than the Cl^-—Cl_2 potential, that is, about −1.2 or −1.3, since chloride ion will partially reduce the +4 complex; and the Ru—$RuCl_5^{--}$ potential must be greater than −0.55 as it is not reduced by iodide. It is, however, reduced by titanous.

Hot nitric acid will not oxidize the +4 complex to the tetroxide but hot perchloric acid does; hence for the $RuCl_5OH^{--}$—RuO_4 potential, −1.5 will be used. On these values the following scheme has been constructed:



$$\begin{array}{ccccccc} 0 & +2 & +3 & +4 & +6 & +7 & +8 \end{array}$$

$$Ru \xrightarrow{-0.45} Ru^{++} \xrightarrow{-0.3} RuCl_5^{--} \xrightarrow{-1.3} RuCl_5OH^{--} \xrightarrow{-1.7} RuO_4^{--} \xrightarrow{-1.6} RuO_4^{-} \xrightarrow{-1.0} RuO_4$$

The ions, Ru^{++}, RuO_4^{--}, and RuO_4^-, are unstable in acid with respect to their own oxidation and reduction, and potentials involving these ions have been chosen to conform with these and certain other facts. All values in this scheme are to be considered as purely tentative, but the author believes that they do permit a coherent interpretation of the chemistry of ruthenium in hydrochloric acid solutions. A similar scheme might be presented for hydrobromic acid, but the principal difference would be a somewhat greater stability of the complex bromides.

For ruthenium in molal alkaline solution, the following potentials appear to conform with the chemical behavior.

$$\begin{tikzcd}
\mathrm{Ru} \arrow[r, dash, "0.35"] \arrow[rr, dash, bend right, "0.3"'] & \mathrm{Ru_2O_3} \arrow[r, dash, "0.2"] & \mathrm{RuO_3^-} \arrow[r, dash, "-0.4"] \arrow[rrr, dash, bend right, "-0.6"'] & \mathrm{RuO_4^{--}} \arrow[r, dash, "-0.6"] & \mathrm{RuO_4^-} \arrow[r, dash, "-1.0"] & \mathrm{RuO_4}
\end{tikzcd}$$

The couple,

$$8OH^- + Ru = RuO_4 + 4H_2O + 8e^-, \qquad E_B^\circ = -0.3$$

should be 0.83 volts greater than the couple in acid solution, and the value of the RuO_4^-—RuO_4 couple should be the same, since H^+ is not involved. The tetroxide appears to oxidize water slowly, but the value -1.0 may be in error by several tenths of a volt. Hypochlorite at 80° C. oxidizes the ruthenate, RuO_4^{--}, to perruthenate, RuO_4^-, and on to the tetroxide which volatilizes from the solution. In general, the estimated values for the alkaline solution are probably not so reliable as those given for the hydrochloric acid solution. The sulfides, Ru_2S_3 and RuS_2, are known but there are no data on their solubilities.

Osmium

The standard state of the element is the solid metal. Based on the estimated values for the heat of sublimation, 125 kcal., and the entropy of sublimation, 44 cal. per degree, an approximate figure for the free energy of the process is 112 kcal.

Oxidation states. In hydrochloric acid, osmium may be present as chlorosmite, $OsCl_6^{---}$, chlorosmate, $OsCl_6^{--}$, and perperosmic acid, H_2OsO_5. These compounds may be classified as belonging to the +3, +4, and +8 states. The +2 ion is unstable in acid and only a few slightly soluble compounds of this state, for example, OsI_2, are known. Complex ions of the +3 and +4 states are formed by Br^-, NO_2^-, $C_2O_4^{--}$, NO, NH_3, and many other groups, but potentials will be considered only in the case of the chlorides. Crowell and Kirschman[22] have presented evidence for the existence, in acid, of unstable halogen derivatives of perosmic acid, $HOsO_4(+7)$, but it is not certain that they were not dealing with osmyl, OsO_2^{++}, derivatives. In alkaline solution the oxides Os_2O_3 and OsO_2 or their hydrates are precipitated from compounds of the +3 and +4 states. The tetroxide forms perperoxmates and although the trioxide of the +6 state has not been isolated, many osmates, for example, K_2OsO_4, are known. A large number of osmyl compounds have been described, but they appear to decompose in acid solutions. There is no evidence of any salts of perosmic acid in alkaline solutions.

The free energy of osmium tetroxide. The only osmium compound for which the heat of formation has been determined is the tetroxide. Bichowsky and Rossini give −93,600 for OsO_4(s). As the molecule is probably tetrahedral, it is possible to estimate an approximate value for the entropy of the gas; the value 68 cal. per degree has been chosen. The vapor pressure of the solid has been measured but the heats of sublimation of Wartenberg[23] and Ogawa[24] are not in good agreement. As a rough value we shall use 25 as the entropy of the solid and calculate ΔS° formation, 81 cal. per degree, and ΔF°, −69,400 cal.

$$4H_2O + Os = OsO_4(s) + 8H^+ + 8e^-, \qquad E^\circ = -0.85$$

The oxide is thus a fairly good oxidizing agent and is reduced to the metal in acid solution by almost all other metals.

Yost and White[25] report

$$H_2OsO_5 = H^+ + HOsO_5^-, \qquad K_1 = 8 \times 10^{-13}$$

The solubility of the oxide in water at 18° C. is given as 0.0186 M. From these data we calculate for the free energy of $HOsO_5^-$, −107,000 cal. and

$$9OH^- + Os = HOsO_5^- + 4H_2O + 8e^-, \qquad E_B^\circ = -0.02$$

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[22] Crowell, W. R., and Kirschman, H. D., J. Am. Chem. Soc., **51**, 1695 (1929); *ibid.*, **54**, 1324 (1932).

[23] Wartenberg, H., Ann., **440**, 97 (1924).

[24] Ogawa, E., Bull. Chem. Soc. Japan, **6**, 302 (1931).

[25] Yost, D. M., and White, R. J., J. Am. Chem. Soc., **50**, 81 (1928).

Potentials of other osmium couples. Although there are no quantitative data, the potentials involving the intermediate oxidation states of osmium are roughly fixed by known reactions of the compounds involved. In making these estimates, the potential of the Os—OsO_4 couple is a valuable aid, as the sum of the potentials of the reduction in steps is determined by this figure. The following scheme summarizes these estimated potentials in 1*M* acid solution:

0 +2 +3 +4 +8

$$\underbrace{Os \xrightarrow{-0.7} Os^{++} \xrightarrow{-0.3} OsCl_6^{---}}_{-0.6} \xrightarrow{-0.85} OsCl_6^{--} \xrightarrow{-1.0} OsO_4(s)$$

A saturated solution of the tetroxide or perperosmic acid is almost as strong an oxidizing agent as is bromine. The $OsCl_6^{--}$ is less powerful, and there is some indication that the reduction to $OsCl_6^{--}$ is slow with certain reducing agents. Since Os^{++} is unstable, the Os—Os^{++} couple must be more negative than the Os^{++}—$OsCl_6^{---}$ couple. Iodide, however, reduces $OsCl_6^{---}$ to form OsI_2, the slight solubility of the latter compound increasing the energy of the reaction.

The reaction

$$3OH^- + HOsO_5^- + OsO_2 = 2OsO_4^{--} + 2H_2O$$

goes as written in 1*M* OH^- but is largely reversed at 10^{-7} *M* OH^-. Upon heating, the dioxide decomposes,

$$2OsO_2 = OsO_4 + Os$$

and the pressure of OsO_4 is said to reach 1 atmosphere at 650° C. From the free energy of OsO_4, we calculate as an approximate value for the free energy of formation of OsO_2, −50,000 cal.

$$5OH^- + OsO_2 = HOsO_5^- + 2H_2O + 4e^-, \qquad E_B^\circ = -0.2$$

With these reactions as a basis, the following scheme of potentials is given for the oxidation states of osmium in alkaline solution:

0 +3 +4 +6 +8

$$\underbrace{Os \xrightarrow{?} Os_2O_3 \xrightarrow{?} OsO_2}_{0.15}\;\underbrace{\xrightarrow{-0.1} OsO_4^{--} \xrightarrow{-0.3} HOsO_3^-}_{-0.2}$$

CHAPTER XV

Manganese, Masurium, and Rhenium

The elements of this group have seven valence electrons, and their electronic configuration in the monatomic gas atoms is s^2d^5 to give a $^6S_{5/2}$ state. Masurium is so rare that quantities sufficient to study its chemistry have not been obtained. The oxidation states of manganese range from +1 to +7 and of rhenium from −1 to +7. Rhenium in the −1 state is the only example of an element in the transition series which is capable of adding an electron.

Manganese

The standard state of the element is the α solid which is stable up to 1108° K. Kelley[1] has given the following data for the sublimation at 25° C.: $\Delta H°$, 69,729 cal.; $\Delta F°$, 59,535 cal.; $\Delta S°$(g), 41.5 cal. per degree.

Oxidation states. Manganese forms compounds of the manganous ion, Mn^{++}, and the manganic ion, Mn^{+++}. The corresponding oxides are basic. The +4 oxide, MnO_2, is amphoteric, but like so many metal dioxides is comparatively inert toward both hydrogen and hydroxide ions. The +6 oxidation state is represented by manganate ion, MnO_4^{--}, which is stable only in alkaline solutions; and the +7 state is represented by permanganate, MnO_4^-. The +1 complex cyanide has been prepared.

Manganous ion and its compounds. Metal amalgam-manganous ion electrodes have been studied, but the potentials obtained have not been reproducible. The value which may be calculated from the third law is probably accurate to 0.03 volts. Bichowsky and Rossini give the $\Delta H°$ of formation of the ion as −49.2 kcal. Assuming the ionic entropy to be the same as ferrous, the free energy of formation of Mn^{++} is −48,600 cal.

$$Mn = Mn^{++} + 2e^-, \qquad E° = 1.05$$

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[1] Kelley, K. K., U. S. Bur. Mines Bull., 383 (1935).

Likewise, using for the hydroxide, $\Delta H^\circ = -1634$ kcal., and assuming 20 cal. per degree for the entropy, the ΔF° is $-143{,}100$ cal.

$$2OH^- + Mn = Mn(OH)_2 + 2e^-, \qquad E^\circ_B = 1.47$$

$$Mn(OH)_2 = Mn^{++} + 2OH^-, \qquad K = 7.1 \times 10^{-15}.$$

Sackur and Fritzmann[2] reported the solubility product to be 4×10^{-14}, and the value 1.3×10^{-18} was given by Britton.[3]

Manganese may be precipitated by cathodic reduction. Allmand and Campbell[4] employed a concentrated manganous sulfate and ammonium sulfate electrolyte. It appears to be necessary to keep the acid concentration low, but if it becomes less than pH 6, considerable oxide forms on the metal surface.

For the solubility product of precipitated manganous carbonate, Ageno and Valla[5] gave 8.8×10^{-11}. From the thermal data we calculate for ΔF° of solution 14,200 cal. and $K = 4 \times 11^{-11}$, but the solubility data are probably the more reliable.

$$CO_3^{--} + Mn = MnCO_3 + 2e^-, \qquad E^\circ = 1.35$$

$$MnCO_3 = Mn^{++} + CO_3^{--}, \qquad K = 8.8 \times 10^{-11}$$

For the formation of manganous sulfide from its elements, the experimental values are: $\Delta H^\circ = -44{,}900$ cal. (by Britzke, *et. al.*[6]) and $\Delta S^\circ = 3.8$. These give for the free energy $\Delta F^\circ = -46{,}000$ cal. and for the solubility product,

$$MnS = Mn^{++} + S^{--}, \qquad K = 5.6 \times 10^{-16}$$

Kolthoff[7] has reported 7×10^{-16}.

Manganic potentials. Except at very low concentrations, manganic ion is unstable with respect to the decomposition,

$$2Mn^{+++} + 2H_2O = MnO_2 + Mn^{++} + 4H^+,$$

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[2] Sackur, O., and Fritzmann, E., Z. Elektrochem., **15**, 845 (1909).

[3] Britton, H. T. S., J. Chem. Soc., **127**, 2118 (1925).

[4] Allmand, A. J., and Campbell, A. N., Trans. Faraday Soc., **20**, 379 (1924).

[5] Cf. Mellor, J. W., *Inorganic and Theoretical Chemistry* (Longmans, New York, 1932), **12**, 437.

[6] Britzke, E. V., Kapustinskii, A. F., and Veselovskii, B. K., J. Phys. Chem. U. S. S. R., **5**, 77 (1934).

[7] Kolthoff, I. M., J. Phys. Chem., **35**, 2720 (1931).

and no very accurate value can be given for the free energy of this reaction. Grube and Huberich[8] gave,

$$Mn^{++} = Mn^{+++} + e^-, \qquad E^\circ = -1.51$$

which is probably correct within 0.1 volt. The heat of formation of the ion, quoted by Bichowsky and Rossini, is obviously for the complex bromide.

A rough value may be calculated for the free energy of formation of the hydroxide, $Mn(OH)_3$. Using $\Delta H^\circ = -221{,}000$ cal. and $\Delta S^\circ = -104$ cal. per degree, the free energy is $\Delta F^\circ = -190{,}000$ cal.

$$OH^- + Mn(OH)_2 = Mn(OH)_3 + e^-, \qquad E^\circ_B = 0.4$$

Employing the value which we shall use for the free energy of the dioxide, we find,

$$2Mn(OH)_3 = Mn(OH)_2 + MnO_2 + 2H_2O,$$

$$\Delta F^\circ = 20{,}600 \text{ cal.}$$

From this free energy, manganic hydroxide appears to be stable with respect to such a decomposition. However this does not prove that it is stable with respect to some manganous manganite, as, for example, $Mn(H_2MnO_4)$, and the substance which we have called manganic hydroxide may indeed be such a complex. The oxidation of manganous hydroxide by oxygen in air is rapid.

No data can be given for the complex halogen ions of +3 manganese or for the complex acetate. Cartledge and Ericks[9] investigated the complex oxalates and found,

$$Mn(C_2O_4)_3^{---} + 2H_2O = Mn(C_2O_4)_2(H_2O)_2^- + C_2O_4^{--},$$

$$K = 3.8 \times 10^{-3} (0^\circ \text{ C.})$$

Complex manganese cyanides. From the work of Grube and Brause[10]

$$Mn(CN)_6^{-4} = Mn(CN)_6^{---} + e^-,$$

$$E^\circ = 0.22.$$

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[8] Grube, G., and Huberich, K., Z. Elektrochem., **29**, 17 (1923).

[9] Cartledge, G. H., and Ericks, W. P., J. Am. Chem. Soc., **58**, 2069 (1936).

[10] Grube, G., and Brause, W., Ber., **60**, 2273 (1927).

The stability of the +3 complex thus greatly reduces the potential of the +2 to +3 couple. The authors also report the formation of a +1 complex with very powerful reducing agents.

$$2CN^- + Mn(CN)_4^{---} = Mn(CN)_6^{-4} + e^-, \qquad E^\circ = 0.7$$

Meyer[11] reported,

$$Mn(OH)_3 + 3CN^- + 3HCN = Mn(CN)_6^{---} + 2H_2O, \qquad K = 2.5 \times 10^{-6} (0^\circ\ C.)$$

Manganese dioxide, manganate, and permanganate. A general lack of agreement is to be noted in the results of numerous investigators who have measured couples involving manganese dioxide. The difficulty appears to be not so much in the irreversibility of a given cell as in the variation of the thermodynamic properties of the dioxide, even when prepared under very similar conditions. Apparently the variation in free energy may be as large as a thousand or more calories, and unfortunately the determined free energies of manganate and permanganate have involved the value for the dioxide. For this reason, we shall use for the free energy of permanganate, the third law value of −100,600 cal., as calculated by Brown, Smith, and Latimer.[12] For the ΔH° of formation of the precipitated MnO_2, Bichowsky and Rossini gave −115,500 cal. The ΔS° is −42.4, and one then computes $\Delta F^\circ = -102{,}900$ cal. We shall use this value, as it probably is as reliable as any, subject to the variations noted above. The free energy of manganate is obtained from the following equilibrium:

$$3MnO_4^{--} + 2H_2O = MnO_2 + 2MnO_4^- + 4OH^-, \qquad \Delta F^\circ = -1640 \text{ cal.}$$

which was studied by Ruby and by Schlesinger and Siems.[13] One then calculates for the formation of manganate ion from its elements, $\Delta F^\circ = -113{,}100$ cal.

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[11] Meyer, J., Z. anorg. Chem., **81**, 385 (1913).

[12] Brown, O. L. I., Smith, W. V., and Latimer, W. M., J. Am. Chem. Soc., **58**, 2144 (1936).

[13] Schlesinger, H. I., and Siems, H. B., J. Am. Chem. Soc., **46**, 1965 (1924).

A number of half-reaction potentials may now be written. Thus for the manganese dioxide-permanganate couple,

$$2H_2O + MnO_2 = MnO_4^- + 4H^+ + 3e^-, \qquad E^\circ = -1.67$$

$$4OH^- + MnO_2 = MnO_4^- + 2H_2O + 3e^-, \qquad E_B^\circ = -0.57$$

Andrews and Brown[14] reported -0.588 for the potential of the alkaline reaction. Other investigators report values of from -0.51 to -0.66. For the E° in acid, the literature contains results ranging from -1.55 to -1.79.

For the manganate-permanganate couple, we calculate,

$$MnO_4^{--} = MnO_4^- + e^-, \qquad E^\circ = -0.54.$$

Sackur and Taegener,[15] from cell measurements, which might be repeated under more favorable conditions, found -0.61.

For the manganese dioxide-manganate couple,

$$4OH^- + MnO_2 = MnO_4^{--} + 2H_2O + 2e^-, \qquad E_B^\circ = -0.58$$

For the manganous-manganese dioxide couple in acid solution,

$$2H_2O + Mn^{++} = MnO_2 + 4H^+ + 2e^-, \qquad E^\circ = -1.28.$$

The value obtained by Brown and Liebhafsky[16] from cell measurements was -1.24. Older values are as high as -1.35.

The $Mn^{++}—MnO_4^-$ couple in acid solution is one of the most important in analytical chemistry. We compute for the overall potential,

$$4H_2O + Mn^{++} = MnO_4^- + 8H^+ + 5e^-, \qquad E^\circ = -1.52$$

The mechanism of a change involving five electrons must obviously be quite complicated. In the important case of the reduction by oxalic acid, the formation of complex oxalate ions of +3 and +4 manganese is probably involved. From the potentials of the various steps, it appears that the +4 to +3 reduction has a low energy, and the formation of a stable +3 complex may have an important bearing on the rate. If the reduction of permanganate in acid solution has to go through the manganate state, the low potential of this step would also constitute a barrier.

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[14] Andrews, L. V., and Brown, D. J., J. Am. Chem. Soc., **57**, 254 (1935).

[15] Sackur, O., and Taegener, W., Z. Elektrochem., **18**, 718 (1912).

[16] Brown, D. J., and Liebhafsky, H. A., J. Am. Chem. Soc., **52**, 2595 (1930).

In this connection it is interesting to note that iodide with an oxidation potential approximately equal to the MnO_4^{--}—MnO_4^- couple reacts instantly with permanganate. Several aspects of the problem have been discussed by Polissar.[17]

From the potential values it may be seen that permanganate will oxidize manganous ion to the dioxide in acid solution; hence reduction of permanganate to manganous ion occurs only with excess of reducing agent. In neutral or alkaline solution the reduction generally stops at the dioxide.

Permanganate is unstable with respect to its reduction by water, and at moderately high acid oxygen is slowly evolved. The reaction in neutral or slightly alkaline solution is not appreciable in several months in the dark but is accelerated by light.

In agreement with the potentials, oxygen will not oxidize manganese dioxide to manganate in aqueous alkaline solution, but the reaction does occur in fused potassium hydroxide. Under these conditions the reaction stops at manganate.

No value can be given for the solubility of the dioxide in acid. The reduction of permanganate to manganous in acid solution may occur without the separation of the dioxide, and an appreciable concentration of +4 manganese doubtless is present, possibly as MnO^{++}. A number of complex ions of the +4 state are known. Manganites are readily formed by fusion of the dioxide with alkalies, but the solubility of the oxide in aqueous hydroxide is very low.

Manganese dioxide electrode in dry cells. It is of interest to discuss the manganese dioxide electrode, used so extensively in dry cells. Inasmuch as the electrolyte is ammonium chloride, it is difficult to write a single net reaction, but the most probable equation (written backward for conformity of $E°$ values) for the electrode reaction appears to be,

$$NH_4OH + Mn(OH)_3 = MnO_2 + NH_4^+ + 2H_2O + e^-,$$

$$E = \text{ca } 0.8$$

Instead of manganic hydroxide, the product may be a mixed +2 and +4 oxide or some solid solution of these oxides. The reaction certainly does not involve the formation of molecular hydrogen on the electrode and its oxidation by the manganese dioxide, as is frequently postulated. The electrode does polarize readily but it is doubtless because of the slow rate of diffusion of the ammonium ion.

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[17] Polissar, M. J., J. Phys. Chem., **39**, 1057 (1935); J. Am. Chem. Soc., **58**, 1372 (1936).

For the reaction at the zinc electrode, we may write,

$$2Cl^- + Zn = ZnCl_2(s) + 2e^-, \qquad E = \text{ca } 0.7$$

By the diffusion of the ammonia, some zinc hydroxide may also be formed. The sum of these half-reaction potentials gives 1.5 volts for the cell potential in agreement with the actual value.

Summary of manganese potentials. The following scheme summarizes the manganese potentials:

ACID SOLUTION

$$\begin{tikzcd}
Mn \arrow[r, no head, "1.05"] & Mn^{++} \arrow[r, no head, "-1.5"] \arrow[rr, no head, bend right, "-1.28"'] & Mn^{+++} \arrow[r, no head, "-1.1"] & MnO_2 \arrow[r, no head, "-2.23"] \arrow[rr, no head, bend right, "-1.67"'] & MnO_4^{--} \arrow[r, no head, "-0.54"] & MnO_4^-
\end{tikzcd}$$

BASIC SOLUTION

$$\begin{tikzcd}
Mn \arrow[r, no head, "1.47"] & Mn(OH)_2 \arrow[r, no head, "0.4"] & Mn(OH)_3 \arrow[r, no head, "-0.5"] & MnO_2 \arrow[r, no head, "-0.58"] \arrow[rr, no head, bend right, "-0.57"'] & MnO_4^{--} \arrow[r, no head, "-0.54"] & MnO_4^-
\end{tikzcd}$$

Rhenium

The standard state of rhenium is the metal. No data have been obtained for its vapor pressure or heat of sublimation.

Oxidation states. Compounds of rhenium corresponding to all of the oxidation states from -1 to $+7$ have been reported. The metal burns in oxygen with the formation of the oxides, Re_2O_7 and ReO_3. The former is soluble in water to form the strong perrhenic acid, $HReO_4$, and the perrhenates are stable in both acid and alkaline solution. The ReO_3 is soluble in alkaline solution but the rhenate ion, ReO_4^{--}, is unstable with respect to its decomposition into perrhenate and the dioxide, ReO_2. The latter is amphoteric but comparatively inert. However, it is more soluble in acids than is manganese dioxide. The sesquioxide, Re_2O_3, is precipitated from solutions which contain Re^{+++} in the form of complex ions, and the $+1$ oxide, Re_2O, is said to be precipitated by the reduction of perrhenate by zinc. The chlorides $ReCl_5$ and $ReCl_3$ may be prepared at high temperatures and the chloro-acids, H_2ReCl_6 and $HReCl_4$, are stable in acid solutions. The pentachloride is unstable in both acid and alkaline solutions, giving perrhenate and the dioxide.

The sulfide, Re_2S_7, may be precipitated from perrhenate solutions by hydrogen sulfide. The sulfide appears to be soluble in excess of sulfide ion, forming thioperrhenate, ReS_4^-. The disulfide, ReS_2, is precipitated by the action of hydrogen sulfide upon $ReCl_6^{--}$.

Zinc in dilute sulfuric acid reduces perrhenate to hydrorhenic acid, HRe.

Rhenium potentials. The only experimental data pertinent to the rhenium potentials which we have is the heat of formation of perrhenate, −224,200 cal. By comparison with the entropy of permanganate and manganese we estimate the entropy of the perrhenate ion to be 50 and that of rhenium to be 8 cal. per degree. The entropy of formation is then −71.7 and the free energy, −202,800 cal.

$$4H_2O + Re = ReO_4^- + 8H^+ + 7e^-, \qquad E^\circ = -0.15$$

$$8OH^- + Re = ReO_4^- + 4H_2O + 7e^-, \qquad E^\circ_B = 0.81$$

The dioxide appears to be stable in acid solution with respect to the decomposition into perrhenate and the metal; hence we shall write,

$$2H_2O + Re = ReO_2 + 4H^+ + 4e^-, \qquad E^\circ = \text{ca } 0.0$$

$$4OH^- + Re = ReO_2 + 2H_2O + 4e^-, \qquad E^\circ = \text{ca } 0.8$$

$$2H_2O + ReO_2 = ReO_4^- + 4H^+ + 3e^-, \qquad E^\circ = \text{ca } -0.3$$

In fairly concentrated hydrochloric acid, iodide reduces perrhenate to chlororhenate,

$$4H_2O + ReCl_6^{--} = ReO_4^- + 6Cl^- + 8H^+ + 3e^-,$$
$$E^\circ = \text{ca } -0.5$$

$$6Cl^- + Re = ReCl_6^{--} + 4e^-, \qquad E^\circ = \text{ca } 0.1.$$

Since the chlororhenite ion is stable,

$$4Cl^- + Re = ReCl_4^- + 3e^-, \qquad E^\circ > 0.1.$$

Lundell and Knowles[18] have prepared rhenide, Re^-, in solution by reduction of perrhenate with zinc in dilute sulfuric acid. Rhenide is readily oxidized, and the following $E°$ value must be reasonably close:

$$Re^- = Re + e^-, \qquad E° = \text{ca } 0.4$$

The potentiometric titration curve given by these authors indicates the presence of Re^+. The $E°$ for the $Re - Re^+$ couple would appear to be about 0.2, but the results are not conclusive.

Summary of rhenium potentials. A summary of these very tentative values for the potentials in acid solution is given below:

$$\begin{tikzcd}
Re^- \arrow[r, dash, "\text{ca } 0.4"] & Re \arrow[r, dash, "\text{ca } 0.2"] \arrow[rrrr, dash, bend left, "-0.15"] \arrow[rrr, dash, bend right, "\text{ca } 0.0"'] & Re^+(?) \arrow[r, dash] & Re^{+++} \arrow[r, dash] & ReO_2 \arrow[r, dash, "\text{ca } -0.3"] & ReO_4^-
\end{tikzcd}$$

It is to be noted that these potentials are much lower than that of the water-oxygen couple, so rhenium in all lower oxidation states is readily oxidized by oxygen to the perrhenate.

In dilute sulfuric acid, perrhenate is cathodically reduced to the metal. The relative concentrations of the intermediate rhenium ions in the reduction process are not known.

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[18] Lundell, G. E. F., and Knowles, H. B., U. S. Bur. Standards J. Research, **18,** 629 (1937).

CHAPTER XVI

Chromium, Molybdenum, Tungsten, and Uranium

The elements of this group have six valence electrons. In the gas atoms both the $s^1d^5(^7S_3)$ and the $s^2d^4(^5D_0)$ states are close together, the lowest energy being in the former state for the two lighter elements and in the latter for the heavier members of the group. The oxidation states range from +2 to +6. With each element the highest state is important, but the lower ones vary considerably in their stabilities with the different elements.

Chromium

The standard state of the element is the solid motal. For the sublimation at 25° C., Kelley[1] has given the following data: $\Delta H°$, 89,368 cal.; $\Delta F°$, 78,627 cal.; and $\Delta S°$, 36.03 cal. per degree.

Oxidation states. Chromium forms compounds having the oxidation numbers +2, +3, and +6. The +2 state is basic. The chromous ion is such a powerful reducing agent that it is not very stable in water solutions even at low hydrogen-ion concentrations. The +3 state is amphoteric, forming compounds of the chromic ion with acids and chromites with bases. Chromium trioxide, CrO_3, is soluble in water. One of the principal characteristics of the trioxides of this group is the formation of polyacids; hence in addition to the chromate ion, CrO_4^{--}, dichromate, $Cr_2O_7^{--}$, and even the tri- and tetrachromates, $Cr_3O_{10}^{--}$ and $Cr_4O_{13}^{--}$, are known. The latter two, however, are not important. A few derivatives of the chromyl ion, CrO_2^{++}, may also be prepared. The blue peroxychromic acid is well known, but there are no data on its reduction potential.

The free energy of chromic ion. Grube and Schlecht[2] and other investigators have sought to measure the potential of the

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[1] Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).

[2] Grube, G., and Schlecht, L., Z. Elektrochem., **32**, 178 (1926); *ibid.*, **33**, 112 (1927).

Cr—Cr^{+++} couple through the intermediate chromous ion. The $E°$ values obtained for the metal-chromic couple are around 0.51. However this value is not in agreement with the thermal data. Choosing the most favorable data, the lowest value one can calculate is 0.67. It seems advisable to assume that the chromium electrode is not reversible and to rely entirely upon the third law calculations, even though these are at best rather sketchy, and a number of our calculated potentials may be in error by 0.1 volts.

Two important chromic ions will be considered. One is the so-called "violet ion" which is generally considered to be $Cr(H_2O)_6^{+++}$ and will be written simply as Cr^{+++}, and the other is the green ion, stable in chloride solutions, $CrCl_2(H_2O)_4^-$, which will be written $CrCl_2^-$. Lamb and Fonda[3] studied the hydrolysis of these ions and reported,

$$Cr^{+++} + H_2O = CrOH^{++} + H^+, \qquad K = 1.5 \times 10^{-4}$$

$$CrCl_2^+ + H_2O = CrOH^{++} + H^+ + 2Cl^-, \qquad K = 1.9 \times 10^{-6},$$

from which one computes,

$$CrCl_2^+ = Cr^{+++} + 2Cl^-, \qquad K = 1.26 \times 10^{-2},$$

$$\Delta F° = 2600 \text{ cal.}$$

Bichowsky and Rossini discuss three values for the heat of formation of $CrCl_2^+$ by different methods which are fairly consistent. We shall use $\Delta H° = -128{,}000$ cal. and assume 28 cal. per degree for the entropy of the ion. This latter value is probably correct to within 5 entropy units. $\Delta F° = -114{,}100$ cal. and

$$2Cl^- + Cr = CrCl_2^+ + 3e^-, \qquad E° = 0.74$$

Similar calculations might be made for the green sulfate and bromide ions. Hundreds of complex chromic ions with the halogen, ammonia, cyanide, thiocyanate, and nitrite are known, but the data are purely qualitative.

Combining with the free energy for the conversion to the purple ion, one computes for the free energy of formation of Cr^{+++}. $-49{,}000$ cal.

$$Cr = Cr^{+++} + 3e^-, \qquad E° = 0.71$$

For a discussion of the electrolytic precipitation of the metal, see dichromate.

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[3] Lamb, A. B., and Fonda, G. R., J. Am. Chem. Soc., **43**, 1155 (1921).

Chromic hydroxide. The formula[4] of the precipitated hydroxide appears to be $Cr(OH)_3 \cdot 3H_2O$. Bjerrum[5] found

$$Cr(OH)_3(ppt) + 2H^+ = Cr(OH)^{++} + 2H_2O, \qquad K = 1 \times 10^8.$$

This, with the constant for the hydrolysis of Cr^{+++}, gives

$$Cr(OH)_3 = Cr^{+++} + 3OH^-, \qquad K = 6.7 \times 10^{-31}$$

and for the free energy of formation of the hydroxide, $\Delta F°$ is ca $-202{,}700$ cal. Although it is difficult to estimate the entropy of the hydrated hydroxide, a value of 55 cal. per degree would make the free energy of precipitation appear to be in reasonable agreement with Recoura's[6] heat of solution, 21,000 cal., of the precipitated hydroxide in acid to give the purple ion. We may then write for the metal-chromic hydroxide couple,

$$3OH^- + Cr = Cr(OH)_3 + 3e^-, \qquad E°_B = 1.3$$

An approximate value for the free energy of chromite may be obtained from the work of Fricke and Windhausen cited above. These authors found that in dilute hydroxide, the ion, CrO_2^-, presumably is found, while at concentrations above 10 M NaOH the principal ion is CrO_3^{---}, but at high concentration of hydroxide the total solubility is low, since the sodium salt is not very soluble. From their solubility data,

$$Cr(OH)_3 + OH^- = CrO_2^- + 2H_2O, \qquad K = 9 \times 10^{-3}$$

$$Cr(OH)_3 = CrO_2^- + H^+ + H_2O, \qquad K = 9 \times 10^{-17}.$$

One computes for the free energy of the ion, CrO_2^-, $-123{,}000$ cal.

$$4OH^- + Cr = CrO_2^- + 2H_2O + 3e^-, \qquad E°_B = 1.2$$

Chromous ion. Grube and Breitinger,[7] by direct cell measurement, found

$$Cr^{++} = Cr^{+++} + e^-, \qquad E° = 0.41$$

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[4] Cf. Fricke, R., and Windhausen, O., Z. anorg. allgem. Chem., **132**, 273 (1924).

[5] Bjerrum, N., Z. physik. Chem., **73**, 740 (1910).

[6] Recoura, A., Compt. rend., **110**, 1029 (1889).

[7] Grube, G., and Breitinger, G., Z. Elektrochem., **33**, 112 (1927).

The free energy of chromous ion then is −39,400 cal. Bennett[8] reported 2×10^{-20} for the solubility product of chromous hydroxide but the value appears to be too small.

Chromate and dichromate. The entropy of chromate ion has been obtained by Smith, Pitzer, and Latimer[9] from the specific heat-temperature curve and the entropy of solution of silver chromate. These authors have calculated for the free energy of formation of chromate ion, −171,400 cal. Neuss and Rieman[10] gave the following data:

$$HCrO_4^- = H^+ + CrO_4^{--}, \qquad K = 3.2 \times 10^{-7},$$
$$\Delta F^\circ = 8850 \text{ cal.}$$
$$Cr_2O_7^{--} + H_2O = 2HCrO_4^-, \qquad K = 2.3 \times 10^{-2},$$
$$\Delta F^\circ = 2240 \text{ cal.}$$

The following ΔF° values for the formation of the ions may be calculated: $HCrO_4^-$, −180,250 cal. and $Cr_2O_7^{--}$, −306,000 cal.

The potentials for the +3 to +6 couples are then determined by the free energies of chromium in the two oxidation states.

$$7H_2O + 2Cr^{+++} = Cr_2O_7^{--} + 14H^+ + 6e^-, \qquad E^\circ = -1.36$$
$$5OH^- + Cr(OH)_3 = CrO_4^{--} + 4H_2O + 3e^-, \qquad E^\circ_B = 0.12$$

Values in the literature are around −1.3 and 0.1 in agreement with these calculations. In $1M$ H^+, dichromate is not a very rapid oxidizing agent and it is difficult to measure the Cr^{+++}—$Cr_2O_7^{--}$ couple directly. Potential measurements in alkaline solution are fairly reproducible, but the reduction probably forms basic chromic chromate, $CrOHCrO_4$, or some other intermediate compound; hence it is not to be expected that the experimental values will be in close accord with our calculated potentials for the alkaline solution. We are unable to give a value for the free energy of the basic chromic chromate. It will be observed that hydrogen ion enters into the equations for the e.m.f. at a high power, and chromic acid in concentrated solutions becomes a very strong oxidizing agent.

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[8] Bennett, W. H., Trans. Faraday Soc., **28**, 889 (1932).

[9] Smith, W. V., Pitzer, K. S., and Latimer, W. M., J. Am. Chem. Soc., **59**, 2642 (1937).

[10] Neuss, J. D., and Rieman, W., J. Am. Chem. Soc., **56**, 2238 (1934).

Metallic chromium may be plated by cathodic reduction from concentrated solutions of chromic acid containing sulfuric acid or chromic sulfate. The reduction process uses up hydrogen ions and a film of the basic chromic chromate appears to be formed on the cathode. In pure chromic acid solutions but little chromium is deposited and hydrogen is liberated. The explanation has been offered[11] that only hydrogen ion can penetrate the chromic chromate diaphragm, but if sulfate is present it in some way acts to break the continuity of the film, and the reduction of the chromium proceeds. The sulfate is thought to aid in stabilizing a layer of chromous ions on the metal surface, which is important as the reduction doubtless goes through this state.

It is difficult to oxidize chromic ion to chromate at a platinum electrode. However, at a lead anode, or if some lead salt is added to the electrolyte, the oxidation is highly efficient. It seems probable that the $Pb^{++}-PbO_2$ couple is involved in the mechanism of the reaction.

Chromyl chloride. The heat of formation of liquid chromyl chloride is given as −134,600 cal. A rough estimate of 50 cal. per degree for the entropy would make the free energy −117,000 cal. One then calculates for the hydrolysis of the liquid,

$$2CrO_2Cl_2 + 3H_2O = Cr_2O_7^{--} + 6H^+ + 4Cl^-, \qquad \Delta F^\circ = -27{,}000 \text{ cal.}$$

This value appears to be reasonable in view of the formation of the chromyl compound by distillation of dichromate with concentrated sulfuric acid in the presence of chloride.

Molybdenum

The standard state of the element is the solid metal. Kelley[12] calculates from the data by Langmuir and his co-workers for the sublimation of molybdenum: ΔH°, 155,493 cal.; ΔF°, 144,571 cal.; ΔS°, 36.7 cal. per degree.

Oxidation states. The most important oxidation state is the +6, and the chemistry of this state is largely that of the oxide, MoO_3, and its compounds. Some idea of the complexity of the polymolybdic acids is gained by the following series of ions, reported by Jander, Jahr, and Heukeshoven[13] as formed by the addition of hydrogen ion to an alkaline molybdate solution: $MoO_4^{--} \rightarrow Mo_3O_{11}^{-4} \rightarrow H(Mo_3O_{11})^{-3} \rightarrow HMo_6O_{21}^{-5} \rightarrow H_2Mo_6O_{21}^{-4} \rightarrow H_3Mo_6O_{21}^{-3} \rightarrow H_7Mo_{12}O_{41}^{-3} \rightarrow H_7Mo_{24}O_{78}^{-5} \rightarrow H_9Mo_{24}O_{78}^{-3} \rightarrow H_{12}Mo_{24}O_{78}$.

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[11] Cf. Miller, E., Z. Elektrochem., **32**, 399 (1926); *ibid.*, **40**, 326 (1934).

[12] Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).

The dioxide, +4 state, is formed at high temperatures, but it is unstable in water solution. The reduction of molybdic acid at low hydrogen-ion concentrations forms the blue oxide, $Mo_3O_8 \cdot 5H_2O$, which is probably $(MoO_2)_2MoO_4$. At high acid, the ions of the +5 state are probably MoO_2^+ or even MoO^{+++}. Further reduction gives the +3 state. The ion Mo^{+++} or MoO^+ appears to be present in the olive-green solutions, and at high concentrations of hydrochloric acid the solution turns red, probably with the formation of $MoCl_6^{---}$. However, Wardlow and Wormell[14] claim that the green and red substances are cis-trans isomers of the formula $MoOCl \cdot 4H_2O$. Although the halogen complex ions of +4 molybdenum do not appear to be stable, the cyanide, $Mo(CN)_8^{-4}$, is known. The solid tetrachloride, $MoCl_4$, has been prepared but it is decomposed in water to give the +3 and the +5 states. The dichloride $MoCl_2$ or Mo_3Cl_6 may be formed at high temperatures. It does not react readily with water but is probably slowly decomposed.

The trisulfide is acidic and dissolves in excess sulfide ion. The solution may be reduced by zinc to the +5 sulfide, Mo_2S_5. The disulfide, MoS_2, exists in nature and the sesquisulfide has been prepared. No thermodynamic data can be given for any of the sulfur compounds.

The free energy of molybdate and molybdic acid. The heat of formation of molybdate is given as −243,500 cal. By comparison with chromate, the estimated entropy of the ion is 14 entropy units. The free energy of formation is then calculated to be −208,000 cal.

$$8OH^- + Mo = MoO_4^{--} + 4H_2O + 6e^-, \qquad E_B^\circ = 0.97$$

Similarly from the heat of formation of the trioxide, −176,500 cal. and its estimated entropy of 17, the free energy is −157,600 cal.

$$Mo + 3H_2O = MoO_3(s) + 6H^+ + 6e^-, \qquad E^\circ = -0.1$$

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[13] Jander, J., Jahr, K. F., and Heukeshoven, W., Z. anorg. allgem. Chem., **194**, 413 (1930).

[14] Wardlow, W., and Wormell, R. L., J. Chem. Soc., 130 (1927).

Although the hydrated oxide is not very soluble in water, the vapor pressure measurements on the hydrate indicate that the free energy of hydration is fairly large. Without implying that the solution actually contains the molecular species H_2MoO_4, we shall write

$$4H_2O + Mo = H_2MoO_4(aq) + 6H^+ + 6e^-, \qquad E^\circ = \text{ca } 0.0$$

The reduction of molybdic acid to the +5 and +3 states. At 1 *M* H^+ the reduction of molybdic acid yields molybdenum blue. As a rough estimate,

$$4H_2O + (MoO_2)_2MoO_4 = 3H_2MoO_4(aq) + 2H^+ + 2e^-, \qquad E^\circ = \text{ca } -0.6$$

$$2H_2O + MoO_2^+ = H_2MoO_4(aq) + 2H^+ + e^-, \qquad E^\circ = \text{ca } -0.4.$$

A powerful reducing agent is required to carry the reduction to the olive green +3 ion. The +3 state is stable with respect to its own oxidation and reduction; and, in keeping with this fact and the overall potential, we estimate,

$$2H_2O + Mo^{+++} = MoO_2^+ + 4H^+ + 2e^-, \qquad E^\circ = \text{ca } 0.0$$

$$Mo = Mo^{+++} + 3e^-, \qquad E^\circ = \text{ca } 0.2$$

Foerster, Fricke, and Hausswald[15] have studied the potentials in hydrochloric acid. Their values for the 2 *N* acid may be summarized in the following scheme:

$$\begin{tikzcd}
\text{Mo}^{+3}(\text{g}) \arrow[r, dash, "0.25"] & \text{Mo}^{+5} \arrow[r, dash, "-0.53"] & \text{Mo}^{+6} \\
\text{Mo}^{+3}(\text{r}) \arrow[ru, dash, "-0.11"] & &
\end{tikzcd}$$

We are unable to assign formulae to the molybdenum chloride complexes in these various oxidation states. The red and green ions of the +3 state have been discussed above. A number of +5 chloride ions are known, for example, $MoOCl_5^{--}$ and $MoOCl_4^-$ and salts of the +6 state, such as $Na(MoO_2Cl_3)$ and $Na_2(MoO_2Cl_4)$, have been prepared. The reduction of molybdic acid to Mo^{+++}

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[15] Foerster, F., Fricke, E., and Hausswald, R., Z. physik. Chem., **146**, 177 (1930).

by passing the acid solution through a Jones reductor (Zn) is a standard quantitative procedure in analytical chemistry.

The hydroxide $Mo(OH)_3$ does not appear to be stable in alkaline solutions.

Molybdenum cyanides. A large number of complex cyanide ions have been reported. Kolthoff and Tomsicek[16] have given the following potential:

$$Mo(CN)_6^{-4} = Mo(CN)_6^{-3} + e^-, \qquad E^\circ = -0.73$$

However, as in the case of the ferro-ferric cyanide couple, the activities of the ions are difficult to obtain and the E° value cannot be accurately calculated from the measured potential.

Molybdenum dioxide. From the heat of formation of the dioxide, −130,000 cal., and the estimated entropy of the oxide, 16 cal. per degree, the free energy is −118,000 cal. This value would make the oxide unstable in alkaline solution,

$$6MoO_2 + 8OH^- = 4\ MoO_4^{--} + 2Mo + 4H_2O, \qquad \Delta F^\circ = -50{,}000 \text{ cal.}$$

Likewise, from our approximate values for the free energies of Mo^{+++}, −13,800 cal., and of H_2MoO_4, −227,000 cal., the oxide also appears to be unstable in acid solution.

$$3MoO_2 + 6H^+ = 2Mo^{+++} + H_2MoO_4(aq) + 2H_2O, \qquad \Delta F^\circ = \text{ca } -14{,}000 \text{ cal.}$$

Molybdenum peroxide. From the heat of formation of the peroxide, MoO_4, in aqueous solution and an estimated entropy, we give as an approximate value

$$H_2MoO_4 = MoO_4(aq) + 2H^+ + 2e^-, \qquad E^\circ = \text{ca } -1.6$$

Tungsten

The standard state of the element is the solid metal. Kelley[17] calculated from the measurements of Langmuir and his co-workers and of Zwikker, for the process of sublimation: ΔH°, 202,660 cal.; ΔF°, 191,500 cal.; and ΔS°, 33.4 cal. per degree.

Oxidation states. The oxides, WO_2, W_2O_5, and WO_3 are well known, although the +5 oxide may be a complex compound containing some WO_3 as its composition approaches the formula W_4O_{11}. Complex ions of the +3 state, such as WCl_5^{--}, may be prepared, but the simple +3 ion is probably unstable. Likewise complex halogen and cyanide ions of the +4 and +5 states exist in water solutions, but there are no simple oxygen ions. None of the lower oxidation states appear to be stable in alkaline solution. Tungstic oxide, like molybdic oxide, forms innumerable complex acids. The normal salts, for example, Na_2WO_4, are readily prepared, but the paratungstates, for example, $Na_{10}W_{12}O_{41}$, are more common. Monotungstic acid, H_2WO_4, does not dissolve appreciably in water, but the paratungstic acid is readily soluble. The trisulfide is acidic, forming thiotungstates, WS_4^{--}, but no quantitative data are available.

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[16] Kolthoff, I. M., and Tomsicek, W. J., J. Phys. Chem., **40**, 247 (1936).

[17] Kelley, K. K., U. S. Bur. Mines Bull., 383 (1935).

Free energies of the oxides. The data on the third-law calculations of the free energies of the tungsten oxides are summarized in Table 30. The entropies of the oxides are estimates.

TABLE 30

FREE ENERGIES OF TUNGSTEN OXIDES

Oxide	Entropy	$\Delta S°$	$\Delta H°$	$\Delta F°$
WO_2	(16)	−41.0	−130,500	−118,300
W_2O_5	(34)	−105.0	−324,000	−293,000
WO_3	(18)	−81.5	−195,700	−171,400

From these free energies, the half-reactions relating the oxides in acid solution may be calculated.

$$2H_2O + W = WO_2 + 4H^+ + 4e^-, \qquad E° = 0.05$$

$$H_2O + 2WO_2 = W_2O_5 + 2H^+ + 2e^-, \qquad E° = 0.00$$

$$H_2O + W_2O_5 = 2WO_3 + 2H^+ + 2e^-, \qquad E° = -0.15$$

These potentials indicate that the lower oxides are stable in acid solution with respect to their decomposition into the metal and the trioxide.

From the recorded heat of formation of the acid, H_2WO_4, one calculates approximately 0.7 for the W_2O_5—H_2WO_4 couple, which is obviously too high. The error apparently lies in the heat of hydration of the oxide as determined by Hüttig.[18]

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[18] Hüttig, G. F., Z. anorg. allgem. Chem., **122**, 44 (1922).

The free energy of tungstate. The calculation of the heat of formation of tungstate involves the same error as that which appears to exist in the calculation of the heat of formation of the acid. Estimating ΔH° as $-256{,}000$ cal. and the entropy of the ion, WO_4^{--}, as 16 by comparison with chromate, the free energy is found to be $-220{,}000$ cal.

$$8OH^- + W = WO_4^{--} + 4H_2O + 6e^-, \qquad E_B^\circ = \text{ca } 1.1$$

This value makes the oxides, WO_2 and W_2O_5, unstable in alkaline solution.

$$3WO_2 + 4OH^- = W + 2WO_4^{--} + 2H_2O, \qquad \Delta F^\circ = \text{ca } -48{,}000 \text{ cal.}$$

$$3W_2O_5 + 10OH^- = W + 5WO_4^{--} + 5H_2O, \qquad \Delta F^\circ = \text{ca } -130{,}000 \text{ cal.}$$

The reduction of tungstate in hydrochloric acid. Collenberg and Guthe[19] studied the reduction of tungstate in concentrated hydrochloric acid. The formulas of the complex ions involved are not known, but those used in the following scheme correspond to salts which have been crystallized from the corresponding solutions:

$$\begin{tikzcd}
W_2Cl_9^{---}(g) \arrow[r, dash, "\text{ca } 0.1"] & WCl_5^- \arrow[r, dash, "\text{ca } 0.1"] & WOCl_4^- \arrow[r, dash, "-0.26"] & WO_2Cl_3^- \\
WCl_5^{--}(r) \arrow[ur, dash, "\text{ca } 0.4"] & & &
\end{tikzcd}$$

The only potential which they were able to measure was for the +5 to +6 step. Solutions containing the red +3 complex readily evolve hydrogen.

Collenberg[20] also obtained a measurement of the potential of the +4—+5 cyanide complex ions.

$$W(CN)_8^{-4} = W(CN)_8^{-3} + e^-, \qquad E = -0.57$$

No accurate E° value can be calculated for ions of such high charge. This potential indicates that the stability of the +4 complex must be very much greater than that of the oxychloride.

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[19] Collenberg, O., and Guthe, A., Z. anorg. allgem. Chem., **136**, 252 (1924).

[20] Collenberg, O., Z. physik. Chem., **109**, 353 (1924).

Uranium

The standard state of the element is the solid metal. There are no data on the vapor pressure of uranium.

Oxidation states. The oxides UO_2 and UO_3, as well as the intermediate oxide U_3O_8 and probably $UO_2 \cdot 2UO_3$ or $U(UO_4)_2$, are stable. The +3 oxide, U_2O_3, does not appear to be stable above 100° C., but the hydroxide $U(OH)_3$ may be precipitated. Complex ions of the +3 and +4 states exist in solution. The pentachloride, UCl_5, is known but is decomposed into complex +4 and +6 ions by water. Hydrates of the trioxide, $UO_3 \cdot H_2O$ and $UO_3 \cdot 2H_2O$, are quite soluble in acids, forming compounds of the uranyl ion, UO_2^{++}. This ion is remarkably stable, and has the properties of a large simple doubly charged metallic ion. Most of its salts are soluble. The addition of alkalies to uranyl solutions precipitates alkali diuranates, for example, $K_2U_2O_7$. The mono-salts may also be prepared—for example, Na_2UO_4. The tendency to form complicated poly-acids, which is characteristic of the trioxides of this group, is somewhat repressed in the case of uranium by the formation of uranyl ion in acid solutions, and by the very slight solubility of the diuranates in general.

Free energy of uranyl ion. From thermal data,

$$U + 2H_2O + 2H^+ = UO_2^{++} + 3H_2, \qquad \Delta H^\circ = -106{,}300 \text{ cal.}$$

We know very little about the entropy of ions such as UO_2^{++} but an estimate of 5 cal. per degree must be fairly close. ΔS° is then 23.8 and ΔF°, −113,400 cal.

$$2H_2O + U = UO_2^{++} + 4H^+ + 6e^-, \qquad E^\circ = 0.82$$

This corresponds to a free energy of formation of −226,800 cal. for UO_2^{++}.

For the solution of the acid, H_2UO_4, in hydrogen ion,

$$H_2UO_4 + 2H^+ = UO_2^{++} + 2H_2O, \qquad \Delta H^\circ = -14{,}850 \text{ cal.}$$

An estimated ΔS° of 11 would make $\Delta F^\circ = -18{,}100$ cal. and

$$UO_2(OH)_2 = UO_2^{++} + 2OH^-, \qquad K = 2 \times 10^{-15}$$

Uranyl ion forms a number of slightly soluble compounds, the more important being: $NH_4UO_2PO_4$, $K_2UO_2Fe(CN)_6$, $Na_4UO_2(CO_3)_3$, $UO_2(IO_3)_2$, and UO_2S. The latter decomposes readily into the dioxide and sulfur. No solubility products can be given for these compounds.

Since the alkali salts are but slightly soluble, the free energies of these salts and not the uranate ions are important in the interpretation of the chemistry of uranium in alkaline solution. Only sodium uranate will be considered. A value for the diuranate would be preferred but the data appear less reliable. Bichowsky and Rossini gave $-500{,}000$ cal. for the heat of formation of the salt Na_2UO_4. A value of 50 cal. per degree is probably within 5 units of the correct entropy. One then computes ΔF° to be $-475{,}000$ cal.

$$2Na^+ + 8OH^- + U = Na_2UO_4 + 4H_2O + 6e^-, \quad E_B^\circ = 2.0$$

Uranium dioxide. A third law calculation for the dioxide, UO_2, using a value of 18 for the entropy of the oxide, gives for ΔF°, $-242{,}200$ cal. For the potentials in acid solution,

$$2H_2O + U = UO_2 + 4H^+ + 4e^-, \quad E^\circ = 1.40$$

$$UO_2 = UO_2^{++} + 2e^-, \quad E^\circ = -0.33$$

Luther and Michie[21] reported,

$$2H_2O + U(SO_4)_2(aq) = UO_2^{++} + 2SO_4^{--} + 4H^+ + 2e^-, \quad E^\circ = -0.42$$

Since the precipitated oxide is readily soluble in sulfuric acid, the agreement between the two potentials is reasonable. Nothing is known regarding the activities of the $U(SO_4)_2$; hence the Luther and Michie value calculated from concentrations is highly approximate.

The free energy calculated for the following reaction would make the oxide stable in alkaline solution with respect to its own oxidation and reduction.

$$3UO_2 + 4Na^+ + 4OH^- = U + 2Na_2UO_4 + 2H_2O, \quad \Delta F^\circ = 63{,}000 \text{ cal.}$$

Uranium in the +3 state. Acid solutions containing uranium in the +4 state may be reduced at a suitable cathode or by zinc to U^{+++} or some complex of this ion. The resulting solutions evolve hydrogen readily; hence we may write, as rough value,

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[21] Luther, R., and Michie, A. C., Z. Elektrochem., **14**, 826 (1908).

$$U^{+3} = U^{+4} + e^-, \qquad E^\circ = \text{ca } 0.5$$

The hydroxide appears to be stable but there are no quantitative data.

Summary of group potentials. In order to compare the potentials of the group as a whole, the following summary is given for the potentials in acid solution.

$$\begin{tikzcd}[column sep=large]
0 & +2 & +3 & +4 & +5 & +6 \\
Cr \arrow[r, dash, "0.86"] \arrow[rr, dash, bend right, "0.71"'] & Cr^{++} \arrow[r, dash, "0.41"] & Cr^{+3} \arrow[rrr, dash, "-1.36"] & & & Cr_2O_7^{--} \\
Mo \arrow[rr, dash, "\text{ca } 0.2"] \arrow[rrrrr, dash, bend right, "0.0"'] & & Mo^{+3} \arrow[rr, dash, "\text{ca } 0.0"] & & MoO_2^+ \arrow[r, dash, "\text{ca } -0.4"] & MoO_3(aq) \\
W \arrow[rr, dash, "<0.05"] \arrow[rrr, dash, bend right, "0.05"'] & & W^{+3} \arrow[r, dash, ">0.05"] & WO_2 \arrow[r, dash, "0.0"] & W_2O_5 \arrow[r, dash, "-0.15"] & WO_3(s) \\
U \arrow[rr, dash, "\text{ca } 1.7"] \arrow[rrr, dash, bend right, "1.40"'] & & U^{+3} \arrow[r, dash, "\text{ca } 0.5"] & UO_2 \arrow[rr, dash, "-0.34"] & & UO_2^{++}
\end{tikzcd}$$

CHAPTER XVII

Vanadium, Columbium, Tantalum, and Protoactinium

The elements of this group have five valence electrons. In monatomic vanadium the lowest electronic state is $d^3s^2(^4F_{3/2})$ and in columbium probably $d^4s^1(^6D_{1/2})$. The lowest state of the two heavier elements is uncertain but is doubtless either the ^4F or ^6D.

Vanadium

The standard thermodynamic state of the element is the solid metal. Bichowsky and Rossini have estimated the heat of sublimation to be 85,000 cal. The entropy of V(g) may be approximated by adding R ln 4 to the value given by the Sackur equation which gives 40.3. $\Delta S°$ of sublimation then is 33.3 cal. per degree and $\Delta F°$, 75,000 cal.

Oxidation states. Vanadium forms the oxides VO, V_2O_3, VO_2 and V_2O_5. The two lower oxides are basic and give the ions V^{++} and V^{+++} in solution. The +4 oxide, often written V_2O_4, dissolves in acids with the formation of vanadyl ion, VO^{++}, and salts of this ion with most acid ions are well known. Although the oxide is not readily soluble in alkalies, vanadites may be prepared, for example, $(NH_4)_2V_2O_5$. The various ions present in solutions of the pentoxide in acids and bases are discussed below. The pentasulfide, V_2S_5, is acidic and dissolves in excess sulfide ion forming thiovanadates. Upon ignition the pentasulfide is reduced to the sesquisulfide, V_2S_3. The +2 sulfide, VS, appears to be formed at high temperatures. No quantitative data can be given for any of these sulfur compounds.

Vanadic acid and the vanadates. The solubility of vanadic oxide in water, as determined by Meyer and Aulich,[1] is 0.0043 M. The determination of the constitution of this solution has been a problem of singular difficulty. The earlier work of Düllberg[2] has been largely verified by the investigations of Bray and Tihenko.[3] The principal negative ion in the solution is $H_2V_6O_{17}^{--}$, that is, the first two steps in the ionization of the corresponding acids are complete. This is in agreement with the ratio of V/H^+ observed by Britton.[4] For the third ionization, Bray and Tihenko found,

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[1] Meyer, J., and Aulich, M., Z. anorg. allgem. Chem., **194**, 282 (1930).

$$H_2V_6O_{17}^{--} = HV_6O_{17}^{---} + H^+, \qquad K = 1.1 \times 10^{-2}$$

and they estimate ca. 10^{-5} for the last step. From this data we could calculate the free energies of these hexavanadate ions in terms of the pentoxide but we can give no absolute values, since, as we shall see, the free energy of formation of the oxide is not accurately known.

Metavanadates, for example, $NaVO_3$, give in solution the ion $V_3O_9^{---}$, the structure probably being a ring of three vanadium and three oxygen atoms alternating with two additional oxygens attached to each vanadium. The coördination number of the vanadium is thus four. With the addition of acid, two of the $V_3O_9^{---}$ ions combine to give $H_2V_6O_{17}^{--}$, but the equilibrium constant has not been obtained.

Orthovanadates, for example, Na_3VO_4, are formed by fusing the oxide with alkalies. In solution they appear to hydrolyze with the formation of the divanadate ion, $V_2O_7^{--}$. In these ions the coördination number of four is again maintained. The divanadate ion is probably unstable with respect to the metavanadate complex, but this is not certain, and the rate of transformation is slow.

The addition of hydrogen ion to a vanadic acid solution forms pervanadyl ion, VO_2^+, or more probably $V(OH)_4^+$. From the solubility of vanadic oxide in nitric acid, determined also by Meyer and Aulich,

$$V_2O_5 + 2H^+ + 3H_2O = 2V(OH)_4^+, \qquad \Delta F^\circ = \text{ca. } 2500 \text{ cal.}$$

Nothing is known regarding the mechanism of the formation of the hexavanadate by the addition of hydroxide to the pervanadyl.

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[2] Düllberg, P., Z. physik. Chem., **45**, 129 (1903).

[3] Bray, W. C., and Tihenko, V. J., (unpublished material, University of California).

[4] Britton, H. T. S., J. Chem. Soc., 1842 (1934).

The vanadyl-pervanadyl couple. From the work of Carpenter,[5] and Coryell and Yost[6]

$$3H_2O + VO^{++} = V(OH)_4^+ + 2H^+ + e^-, \qquad E^\circ = -1.000.$$

Vanadic acid at 1 *M* hydrogen ion is thus a fairly powerful oxidizing agent and is converted to vanadyl by moderately strong reducing agents.

The V^{+++}—VO^{++} and V^{++}—V^{+++} couples. Foerster and Böttcher[7] report,

$$H_2O + V^{+++} = VO^{++} + 2H^+ + e^-, \qquad E^\circ = -0.314$$

$$V^{++} = V^{+++} + e^-, \qquad E^\circ = 0.20.$$

The solubilities of the hydroxides, $VO(OH)_2$, $V(OH)_3$, and $V(OH)_2$, are not known; hence no values can be given for any of the vanadium couples in alkaline solution. However all these hydroxides appear to be stable with respect to their own oxidation and reduction. Vanadous ion is a powerful reducing agent and the vanadous hydroxide is extremely powerful. This seems to indicate that the vanadic hydroxide is much less soluble than the vanadous.

The free energy of the vanadium oxides. The heat of combustion of vanadium to give a mixture of oxides has been determined. From this and other data Bichowsky and Rossini have calculated the following ΔH° values: V_2O_2, -195 kcal.; V_2O_3, -330 kcal.; V_2O_4, -383 kcal.; V_2O_5, 437 kcal. Since the entropies are known, a computation gives the following corresponding ΔF° values in calories: $-182{,}000$, $-311{,}000$, $-357{,}000$ and $-406{,}000$. The potentials relating the various oxides and the metal in acid solution are given by the following scheme:

$$V \overset{0.75}{\overline{\qquad\qquad}} V_2O_2 \overset{1.57}{\overline{\qquad\qquad}} V_2O_3 \overset{-0.23}{\overline{\qquad\qquad}} V_2O_4 \overset{-0.17}{\overline{\qquad\qquad}} V_2O_5$$

Since the oxides are soluble in acids, the potentials, at least in the thermodynamic sense, have little chemical significance. However, we wish to point out that on the basis of any reasonable assumptions regarding the free energies of solution of the oxides, these potentials cannot be brought into agreement with the values given above from direct cell measurements. We are therefore forced to conclude that the errors in the heats of formation must be unusually large.

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[5] Carpenter, J. E., J. Am. Chem. Soc., **56**, 1847 (1934).

[6] Coryell, C. D., and Yost, D. M., J. Am. Chem. Soc., **55**, 1909 (1933).

[7] Foerster, F., and Böttcher, F., Z. physik. Chem., **A151**, 321 (1930).

The metal—V^{++} couple. If we accept the free energy of vanadium pentoxide, calculated above, and the free energy of solution of the oxide in acid, the $E°$ value for the $V—V^{++}$ couple would be approximately 1.8. On the other hand the probable energy of hydration of V_2O_2 and the solubility of the +2 hydroxide would give about 1.2. On this basis we shall write,

$$V = V^{++} + 2e^-, \qquad E° = 1.5 \pm 0.3$$

The metal cannot be precipitated by cathodic reduction in acid or neutral solutions but probably can be reduced from the hydroxide, $V(OH)_2$.

Vanadium peroxyacids. Hydrogen peroxide forms both mono- and diperoxyacids with vanadium, and in high acid at least one of the acids gives a positive peroxy ion. Heats of the reactions have been measured but the formulas of the compounds are too uncertain to permit an estimation of the reaction entropies.

Columbium

The standard state of columbium is the metal. No data can be given for the heat or free energy of sublimation.

Oxidation states. The +5 oxidation state, as represented by columbic oxide, Cb_2O_5, is similar to vanadium in the types of acid ions which are formed. The +4 oxide, CbO_2, is known but it is difficult to prepare. Solutions containing the ion, Cb^{+++}, or complexes of this ion, are made by cathodic reduction or by reduction with zinc, of solutions of columbic oxide in sulfuric, hydrochloric, or hydrofluoric acids. The complex ammonium sulfate has been isolated. It is doubtful if the hydroxide, $Cb(OH)_3$, has been obtained in the pure state, as basic salts appear to be precipitated by alkalies. The oxidation state of the chloride formed by the reduction of the pentachloride by sodium at high temperature is still uncertain. The earlier formula, $[Cb_6Cl_{12}]Cl_2 \cdot 7H_2O$, which was assigned to the substance extracted by water, is more likely $H[Cb_3Cl_7H_2O]3H_2O$ but there is some doubt about the columbium being present in the +2 state. The formula may be $(Cb_3Cl_7O)3H_2O$.

At least two peroxycolumbic acids have been prepared. The formulas assigned are $HCbO_4$ and H_3CbO_8, but there are no data for their free energies. Hydrogen sulfide appears to have no action upon columbic acid or columbates.

Columbic oxide. The oxide is less soluble in water than is vanadic oxide; but, like the latter, it is much more soluble in concentrated acids. Kiehl and Hart[8] found that the solubility in $3M$ H_2SO_4 was about $0.038M$ Cb_2O_5. The solution may contain the ion $Cb(OH)_4^+$, but in more concentrated sulfuric acid probably forms a complex sulfate. The solution in hydrofluoric acid gives salts with the alkalies such as K_2CbOF_5 and $KCbF_6$.

Ortho- and metamonocolumbates, and di- and hexacolumbates similar to the corresponding vanadates, are known and it seems probable that the conclusions drawn concerning the relation between the meta- and hexavanadate ions in solution also holds true for these columbate ions. This is substantiated by the results of Süe[9] who reports the precipitated hydrate, $3Cb_2O_5 \cdot 2H_2O$ or $H_4Cb_6O_{17}$. This is probably the formula of the acid in solution. There are no data on the ionization constants of the acid but it is doubtless somewhat weaker than vanadic acid. Süe gave some data for the hydrolysis of columbate solutions.

Columbium potentials. Becker and Roth[10] report for the heat of combustion of columbium to form the pentoxide, −463,100 cal. An estimate of −125 cal. per degree for $\Delta S°$ of the reaction would give for the free energy of formation of the oxide −425,800 cal. One then computes for the Cb—Cb_2O_5 couple in acid solution

$$5H_2O + 2Cb = Cb_2O_5 + 10H^+ + 10\,e^-, \qquad E° = 0.62$$

Kiehl and Hart[11] measured the e.m.f. of the Cb^{+3}—Cb^{+5} couple in various concentrations of sulfuric acid against a saturated potassium chloride calomel electrode. Using $3.14M$ H_2SO_4 and equal concentrations of columbium in the two oxidation states, they found for the cell 0.373; and for $9.87M$ H_2SO_4, 0.426. It is difficult to account for the increase in potential at higher acid concentrations unless the +5 columbium forms a very stable complex with sulfate ion. The formula of this ion is not known but we will assume $CbO(SO_4)_2^-$ and write as an approximate value,

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[8] Kiehl, S. J., and Hart, D., J. Am. Chem. Soc., **50**, 1608 (1928).

[9] Süe, P., Compt. rend., **194**, 1745 (1932).

[10] Becker, G., and Roth, W. A., Z. physik. Chem., **A167**, 16 (1933).

[11] Kiehl, S. J., and Hart, D., J. Am. Chem. Soc., **50**, 2337 (1928).

$$2SO_4^{--} + H_2O + Cb^{+++} = CbO(SO_4)_2^- + 2H^+ + 2e^-, \qquad E° = 0.1$$

From the solubility data for columbic oxide in sulfuric acid by Kiehl and Hart, cited above, the free energy of solution of the oxide must be around 3000 cal. Hence, for the overall potential for the $Cb—CbO(SO_4)_2^-$ couple,

$$H_2O + 2SO_4^{--} + Cb = CbO(SO_4)_2^- + 2H^+ + 5e^-, \qquad E° = 0.60$$

and the potential for the $Cb—Cb(OH)_4^+$ couple is probably the same order of magnitude. This then gives,

$$Cb = Cb^{+++} + 3e^-, \qquad E° = \text{ca } 1.1$$

Ott[12] reported the formation of the dioxide, CbO_2, by the reduction of solution of the complex fluoride, K_2CbOF_5; but Kiehl and Hart found no evidence for the +4 state. These authors stated that the +3 state was brown in concentrated acid solutions but became blue upon dilution, without change in the equivalents of reducing power.

No values can be given for the columbium potentials in alkaline solution. Isgarischew and Kaplan[13] reported the cathodic reduction of columbium in solutions of potassium hydroxide and oxalic acid with the formation of a mixture of the metal and intermediate solids which were not further reduced.

Tantalum

The standard state of tantalum is the metal. There are no data on the sublimation process.

Oxidation states. The only important compounds of tantalum are the oxide and halides of the +5 oxidation state and their derivatives. There is some evidence of the dioxide, TaO_2. When the pentachloride is heated with sodium and the resulting product extracted with water, a soluble complex is formed. Lindner[14] offers evidence in favor of the formula $H[Ta_3Cl_7H_2O]3H_2O$, which is a compound of the +2 oxidation state. However, Ruff and Thomas[15] believe the formula to be $(Ta_3Cl_7O)3H_2O$, that is, a compound of the +3 state.

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[12] Ott, F., Z. Elektrochem., **18**, 349 (1912).

[13] Isgarischew, N., and Kaplan, G. E., Z. Elektrochem., **40**, 33 (1934).

[14] Lindner, K., Z. anorg. allgem. Chem., **160**, 57 (1927).

The disulfide, TaS_2, is formed at high temperatures by direct union of the elements. When heated in water it forms the pentoxide, hydrogen, and hydrogen sulfide. There is no reaction between sulfide ion and tantalates in solution.

Hydrogen peroxide acts upon tantalates to form peroxytantalates. Salts of the acids $HTaO_4$ and H_3TaO_8 have been reported but no energy data can be given.

Tantalic oxide and fluoride. The oxide Ta_2O_5 is practically insoluble in perchloric or nitric acids. It dissolves slightly in sulfuric acid and more readily in oxalic acid, doubtless with the formation of complex sulfate and oxalate ions. No quantitative data have been obtained for any of these solubilities.

With alkalies, tantalates are formed, the most important being derivatives of hypothetical hexa-acids, for example, $(NH_4)_2Ta_6O_{16}\cdot 5H_2O$ and $Na_8Ta_6O_{19}\cdot 25H_2O$.

The pentafluoride TaF_5 forms by direct combination of the elements. It, and also the oxide, are soluble in hydrofluoric acid to give complex fluo-acids. Common potassium salts are $KTaF_6$, K_2TaF_7, and $KTaOF_4$.

Tantalum potentials. Becker and Roth[16] found −484,500 cal. for the heat of formation of the oxide. Estimating $\Delta S°$ as −125 cal. per degree, the free energy of formation is −447,200 cal. This gives for the Ta—Ta_2O_5 couple,

$$5H_2O + 2Ta = Ta_2O_5 + 10H^+ + 10\,e^-, \qquad E° = 0.71$$

Hevesy and Slade[17] studied the potential of the Ta—TaF_5 couple. They reported that tantalum in the passive state was more electronegative than silver and, when active, about like copper. From the potential calculated above and the solubility of the oxide in hydrofluoric acid, it is obvious that their electrode, even in its active state, was far from the equilibrium potential.

No values can be given for the couple in alkaline solution. Except for the complex chloride, noted above, which was prepared by reduction at high temperature, there is no evidence of the existence of tantalum in lower oxidation states in water solutions.

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[15] Ruff, O., and Thomas, F., Z. anorg. allgem. Chem., **148**, 19 (1925).
[16] Becker, G., and Roth, W. A., Z. physik. Chem., **A167**, 16 (1933).
[17] Hevesy, G. von, and Slade, R. E., Z. Elektrochem., **18**, 1001 (1912).

Protoactinium

Protoactinium, with a half-life of about 32,000 years, is, next to radium, the longest lived radioactive product of the disintegration of uranium. Grosse[18] has isolated a few tenths of a g of the element. Although no quantitative values are yet available, the following facts are of interest. The metal is not readily oxidized in air. The pentoxide, Pa_2O_5, is more basic than the corresponding tantalum oxide, and the hydrated oxide dissolves appreciably in sulfuric acid, probably with the formation of PaO_2^+. No protoactinates are formed by fusion of the oxide with sodium carbonate. The element is precipitated from acid solution by the formation of the peroxyacid and by the addition of phosphoric acid. The pentachloride is formed at 500° C. by the reaction,

$$Pa_2O_5 + 5COCl_2 = 2PaCl_5 + 5CO_2$$

and the metal was prepared by the decomposition of the chloride by heating on a tungsten filament in a high vacuum.

Summary of group potentials. For ease in comparison, the following summary of group potentials in acid solution is given:

$$\begin{tikzcd}
V \arrow[r, dash, "\text{ca } 1.5"] & V^{+2} \arrow[r, dash, "0.20"] & V^{+3} \arrow[r, dash, "-0.31"] & VO_2^+ \arrow[r, dash, "-1.00"] & V(OH)_4^+
\end{tikzcd}$$

$$\begin{tikzcd}
Cb \arrow[r, dash, "\text{ca } 1.1"] \arrow[rr, dash, bend right, "0.62"'] & Cb^{+3} \arrow[r, dash, "\text{ca } 0.1"] & Cb_2O_5
\end{tikzcd}$$

$$\begin{tikzcd}
Ta \arrow[r, dash, "0.71"] & Ta_2O_5
\end{tikzcd}$$

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[18] Grosse, A. von, J. Am. Chem. Soc., **52**, 1745 (1930); *ibid.*, **56**, 2501 (1934).

CHAPTER XVIII

Titanium, Zirconium, Hafnium, and Thorium

The elements of this group have four valence electrons d^2s^2, and the lowest electronic state in the gaseous atoms is the $^3F_2$. The most important oxidation state is the +4, and for the three heavier elements this is the only state which is stable in solutions. Thorium forms a tetrahydrogen compound but it appears to be a real hydride; hence the oxidation state of the thorium is also +4 in this compound.

Titanium

The standard thermodynamic state of titanium is the solid metal. No experimental data are available regarding the heat and free energy of sublimation, but Bichowsky and Rossini estimated 100,000 cal. for the ΔH°.

Oxidation states. Titanium forms compounds of the +2, +3, and +4 oxidation states. The oxides of all three states are known but only the dioxide, TiO_2, is stable in contact with water. The spectrum of the monoxide is common in the light from certain types of stars. The two lower oxides are basic and the dioxide is amphoteric. The tetrafluoride is acidic and forms salts of the type K_2TiF_6, and the trifluoride is also slightly acidic. The soluble peroxy-acid, H_2TiO_4, is well known but no thermodynamic data for it are available.

Titanium dioxide. Bichowsky and Rossini gave for the heats of formation of the dioxide, 218.0 kcal. for rutile and 214.1 kcal. for the amorphous form. Estimating the entropy of formation as −42.5 cal. per degree, the corresponding free energies are −205,300 and −201,400 cal. For the Ti—TiO_2 couple, one calculates,

$$2H_2O + Ti = TiO_2(\text{amorp}) + 4H^+ + 4e^-, \qquad E^\circ = 0.95$$

The titanium electrode is highly irreversible and no direct measurements of the potential can be made.

The unhydrated oxide does not dissolve appreciably in either acids or bases but the hydrated forms are somewhat soluble in both. The two hydrates, $TiO_2 \cdot H_2O$ and $TiO_2 \cdot 2H_2O$ are known. There are no data on the free energies of hydration or of solution. From the qualitative reactions the following highly approximate estimates are made:

$$TiO_2(\text{amorp}) + H_2O = TiO(OH)_2, \qquad \Delta F^\circ = \text{ca } -2500 \text{ cal.}$$

$$TiO(OH)_2 = TiO^{++} + 2OH^-, K = \text{ca } 10^{-30}$$

The approximate value for the free energy of titanyl ion, TiO^{++}, is $-144{,}400$ cal. Assuming that the principal ion in one molal acid is titanyl, the overall potential of the Ti—TiO^{++} couple is calculated to be the same as that for the dioxide,

$$H_2O + Ti = TiO^{++} + 2H^+ + 4e^-, \qquad E^\circ = \text{ca } 0.95$$

Even the qualitative data on the solubility of the hydrated oxide in alkalies are conflicting, and no values will be given for the formation of the titanate ions. The common salts are derivatives of the meta-acid, for example, Na_2TiO_3, but di-, tri-, and penta-titanates are also known.

The Ti^{+3}—TiO^{++} couple. Diethelm and Foerster[1] studied the potential of solutions containing +3 and +4 titanium. For equal concentrations of the two ions in 4.1 *N* H_2SO_4 they found $E = -0.056$. Although they calculated their results for the ions, Ti^{+3} and Ti^{+4}, the potential was a function of the hydrogen ion, becoming more negative with higher acid concentration. Without attempting to recalculate their results in terms of activities, we shall write,

$$H_2O + Ti^{+3} = TiO^{++} + 2H^+ + e^-, \qquad E^\circ = \text{ca } -0.1$$

From high temperature measurements on the reduction of titanium dioxide by hydrogen, Nasu[2] has given,

$$2TiO_2 + H_2 = Ti_2O_3 + H_2O, \qquad \Delta F^\circ = 5280 \text{ cal.}$$

This is in agreement with the potential in the water solution, if we assume

$$\tfrac{1}{2}Ti_2O_3 + \tfrac{3}{2}H_2O = Ti^{+++} + 3OH^-, \qquad K = \text{ca } 10^{-40}.$$

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[1] Diethelm, B., and Foerster, F., Z. physik. Chem., **62**, 129 (1908).
[2] Nasu, N., J. Chem. Soc. Japan, **56**, 659 (1935).

This value for K appears quite reasonable. The free energy of the sesquioxide, calculated from our value for the dioxide, is −340,800 cal. The oxide is obviously unstable in water with respect to the evolution of hydrogen. Experimentally this instability increases in alkali. The reduction of titanyl in acid solution is readily accomplished by zinc or electrolytically.

The Ti^{++}—Ti^{+3} couple. Forbes and Hall[3] prepared a mixture of the chlorides, $TiCl_2$ and $TiCl_3$, by the action of hydrogen chloride upon finely divided titanium, and measured the potential of the couple at 0° C., using a mercury electrode. They gave for the $E°$ at 0° C., 0.37 volts. Although entropy of the reaction (with H_2—H^+ couple) is about 15 units, we shall not make the temperature correction but will give as an approximate value the same potential at 25° C.

$$Ti^{++} = Ti^{+++} + e^-, \qquad E° = 0.37.$$

Considering the reactivity of the Ti^{++} ion, this potential appears to be lower than one would expect. However, it may be that the ion is simply a more rapid reducing agent. At any rate, it is impossible to have appreciable concentrations of +2 titanium in solutions which have an acidity greater than 0.1 N H^+.

The +2 hydroxide, $Ti(OH)_2$, is less stable than the positive ion and readily evolves hydrogen. This is to be expected inasmuch as the solubility of the +2 hydroxide is doubtless much greater than that of the +4.

The Ti—Ti^{++} potential. From the potentials relating TiO^{++} to the metal and to the lower oxidation states, we may now calculate,

$$Ti = Ti^{++} + 2e^-, \qquad E° = 1.75.$$

In agreement with this very positive value, titanium can not be precipitated by cathodic reduction in water solutions. However, the metal is very passive and is not readily oxidized by mild oxidizing agents.

Fluotitanate. Titanium dioxide dissolves in hydrofluoric acid with the formation of the fluotitanate, TiF_6^{--}. From the heat of formation, −557,500 cal., we may make a rough calculation of its free energy, using the estimated entropy of the ion as 20 cal.

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[3] Forbes, G. S., and Hall, L. P., J. Am. Chem. Soc., **46**, 385 (1924).

per degree. The value is $-508{,}700$ cal. This gives for the metal-fluotitanate couple,

$$6F^- + Ti = TiF_6^{--} + 4e^-, \qquad E^\circ = 1.24.$$

Solid fluotitanites, such as $(NH_4)_2TiF_5$, have been prepared, but there is no evidence of their formation in solution by reduction of the $+4$ complex.

Summary of titanium potentials. The following scheme summarizes the titanium potentials in acid solutions:

$$\underbrace{\mathrm{Ti}\overset{1.75}{\text{———}}\mathrm{Ti}^{++}\overset{0.37}{\text{———}}\mathrm{Ti}^{+++}\overset{-0.1}{\text{———}}\mathrm{TiO}^{++}}_{0.95}$$

Zirconium

The standard state of zirconium is the solid metal. Bichowsky and Rossini estimate the heat of sublimation to be 110,000 cal.

Oxidation states. The only oxidation state stable in water solutions is the $+4$. The dioxide is somewhat more basic than titanium dioxide and, when hydrated, dissolves fairly readily to form the zirconyl ion, ZrO^{++}. The solubility of the oxide in alkaline solution is slight and the zirconates are much less stable than the titanates. The tetrafluoride forms numerous fluozirconates, for example, Na_2ZrF_6, but their thermodynamic properties have not been studied. Around 250° C., solid zirconium tetrachloride is reduced by powerful metallic reducing agents to the $+3$ and $+2$ chlorides. Hydrogen is evolved by the reaction of these chlorides with water.

The free energy of zirconium dioxide. Based on the heat of formation of the monoclinic dioxide, $-258{,}100$ cal., and the estimated entropy of the reaction, -42.5 cal. per degree, the free energy of formation is $-245{,}400$ cal.

$$2H_2O + Zr = ZrO_2 + 4H^+ + 4e^-, \ E^\circ = 1.43.$$

Bichowsky and Rossini select $-198{,}300$ cal. as the best value for the heat of formation of zirconyl ion, ZrO^{++}. Taking the entropy of the ion as zero, one then computes,

$$Zr + 2H^+ + H_2O = ZrO^{++} + 2H_2, \qquad \Delta H^\circ = -129{,}000 \text{ cal}$$

$$\Delta F^\circ = -141{,}400 \text{ cal.}$$

This gives for the free energy of zirconyl ion, −198,100 cal.

$$H_2O + Zr = ZrO^{++} + 2H^+ + 4e^-, \quad E^\circ = 1.53$$

From the hydrogen electrode titration curves obtained by Britton[4] a rough value may be given for the solubility constant of the hydrated dioxide,

$$ZrO(OH)_2(s) = ZrO^{++} + 2OH^-, \qquad K = \text{ca } 1 \times 10^{-26}$$

One then calculates for the free energy of hydration,

$$ZrO_2 + H_2O = ZrO(OH)_2(s), \qquad \Delta F^\circ = \text{ca } -5500 \text{ cal.}$$

There is no experimental value for this free energy, but the hydrate decomposes at around 200° C.; hence the calculated free energy must be fairly close. The corresponding free energy of formation of the hydrate is −307,600 cal.

The solubility of the hydrated oxide was reported by Venable and Clark[5] as 6×10^{-4} moles per liter of H_2ZrO_3 in 2.5 *M* KOH. The formula of the zirconate in solution is not known, but we shall write

$$H_2ZrO_3(s) + OH^- = HZrO_3^- + H_2O, \qquad K = \text{ca } 10^{-4}$$

$$4OH^- + Zr = H_2ZrO_3 + H_2O + 4e^-, \qquad E^\circ_B = 2.32$$

Solid zirconates, such as Na_2ZrO_3, Na_4ZrO_4, and $Li_2Zr_2O_5$, have been prepared by fusion of the oxide with alkalies.

Zirconyl hydrogen phosphate, $ZrO(HPO_4)_2$, is very sparingly soluble. Hevesy and Kimura[6] reported its solubility as 1.2×10^{-4} moles per liter in 6 *N* HCl.

Zirconium disulfide, ZrS_2, and zirconyl sulfide, ZrOS, have been prepared at high temperatures, but neither of these sulfides can be precipitated from water solutions.

Zirconyl oxalate, $ZrOC_2O_4$, is precipitated from acid solutions by oxalic acid, the precipitate is soluble in excess oxalic acid and in ammonium oxalate with the formation of complex oxalate ions, but no quantitative data can be given.

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[4] Britton, H. T. S., J. Chem. Soc., **127**, 2135 (1925).

[5] Venable, F. P., and Clark, T., J. Am. Chem. Soc., **18**, 434 (1896).

[6] Hevesy, G. von, and Kimura, K., J. Am. Chem. Soc., **47**, 2540 (1925).

Hafnium

The standard state of hafnium is the solid metal. The heat and free energy of sublimation have not been determined, but they must be slightly greater than the corresponding values for zirconium.

Oxidation states. Only compounds of the +4 oxidation state are known. No reduction of the oxide or halides, even at high temperatures, has been reported. The similarity of +4 compounds of hafnium and zirconium is remarkable, and the difficulties of separation are comparable to the separation of neighboring elements of the rare earth group. A few slight differences in the properties of compounds of the two elements may be noted. Hafnyl chloride is somewhat less soluble in concentrated hydrochloric acid than is zirconyl chloride. The ammonium hexofluohafniate is slightly more soluble at 0° C. than is the fluozirconate. Hafnium salicylate is less soluble than zirconium salicylate. In general the reactions of hafnium indicate that the oxide is slightly more basic than is zirconium oxide; hence, hafnyl compounds hydrolyze to a greater extent, and the compounds with acid oxides, for example, $HfOSO_4$ and $HfO(NO_3)_2$, decompose into their respective oxides at slightly higher temperatures.

The free energy of hafnium oxide. From the heat of formation of the dioxide, −271,500 cal. and the estimated entropy of the reaction, −42.5 cal. per degree, one calculates −258,200 cal. for the free energy of formation. The potential of the Hf—HfO_2 couple in acid solution then is,

$$2H_2O + Hf = HfO_2 + 4H^+ + 4e^-, \qquad E^\circ = 1.57$$

There are no data on the heat or free energy of formation of hafnyl ion, HfO^{++}. However, we shall assume that the free energy of hydration of the oxide is the same as for zirconium dioxide and that the oxide is slightly more basic, and write,

$$HfO_2 + H_2O = HfO(OH)_2, \qquad \Delta F^\circ = -5500 \text{ cal.}$$

$$HfO(OH)_2 = HfO^{++} + 2OH^-, \qquad K = \text{ca } 10^{-25}.$$

One then calculates for the free energy of formation of hafnyl ion, −212,100 cal., and for the Hf—HfO^{++} couple,

$$H_2O + Hf = HfO^{++} + 2H^+ + 4e^-, \qquad E^\circ = 1.68.$$

The free energy of solution of the hydrated oxide in alkali is doubtless closely the same as the value for the zirconium oxide. Since the solubility is small, we shall write for the potential in alkaline solution,

$$4OH^- + Hf = HfO(OH)_2 + H_2O + 4e^-, \quad E_B^\circ = 2.60.$$

The status of the data pertaining to the sulfides, phosphates, and oxalates is similar to that for zirconium.

Thorium

The standard state of thorium is the solid metal. Bichowsky and Rossini estimate 177 kcal. as the heat of sublimation of the metal.

Oxidation states. The only stable oxidation state is the +4. The dioxide ThO_2 is much more basic than the dioxides of the lighter elements of the group and shows no tendency to form thorates even when fused with alkalies. The hydrated oxide dissolves readily in strong acids, and the hydrated normal salts may be crystallized from the solutions, for example, $Th(SO_4)_2 \cdot 8H_2O$ and $Th(NO_3)_4 \cdot 12H_2O$. The addition of alkalies to these solutions precipitates basic salts, for example, $ThOSO_4 \cdot H_2O$ and $Th(OH)_2Cl_2 \cdot 4H_2O$. Double salts of almost every negative ion may also be prepared, for example, $K_4Th(SO_4)_2 \cdot 2H_2O$ and $KTh(NO_3)_5 \cdot 9H_2O$. The tetrafluoride, $ThF_4 \cdot 4H_2O$, may be precipitated. Sodium carbonate precipitates $ThOCO_3 \cdot 8H_2O$, soluble in excess of the reagent. Oxalic acid precipitates the oxalate, which is soluble in ammonium oxalate. Other slightly soluble compounds are the iodate, $Th(IO_3)_4$, and the phosphate, $Th_3(PO_4)_4 \cdot 4H_2O$. The heats of precipitation of many of these compounds have been measured, but the data can not be used to calculate solubility products inasmuch as little is known regarding the activities or entropies of the ions in solution. Sulfides are formed only at high temperatures. A slightly soluble peroxy-acid is precipitated from dilute acid solutions by hydrogen peroxide. The formula is probably H_2ThO_4, with an indefinite amount of water.

Free energy of thorium dioxide. The thermal data may be used to calculate a value for the free energy of formation of the dioxide, which should be fairly accurate. The data are: ΔH°,

−293,000 cal.; $\Delta S°$, 43.0 cal. per degree, and $\Delta F°$, −280,100 cal. One then computes for the Th—ThO_2 couple in acid solution,

$$2H_2O + Th = ThO_2 + 4H^+ + 4e^-, \qquad E° = 1.80$$

It is difficult to know how to proceed to obtain a free energy for thorium ion in solution. The Bichowsky and Rossini value for the heat of formation of the hydroxide is inconsistent with their other data, and their approximate value for the ion, Th^{+4}, obtained from the chloride, cannot be corrected for complex ion formation. Hydrogen electrode titration curves have been investigated, but the formation of basic precipitates renders it impossible to use them to estimate the solubility of the hydroxide in acid.

A very rough value will be obtained by the following method. From comparison with other free energies of hydration we estimate,

$$ThO_2 + 2H_2O = Th(OH)_4, \qquad \Delta F° = \text{ca } -15{,}000 \text{ cal.}$$

The heat of solution of the hydroxide in nitric acid is given by Pissarjewsky[7] as −29,900 cal. There is probably a fairly large correction to the infinitely dilute solution for his value which we cannot make. For the entropy of solution we shall use −72 cal. per degree, and this may also involve a large error. One then calculates,

$$Th(OH)_4 + 4H^+ = Th^{+4} + 4H_2O, \qquad \Delta F° = -8400 \text{ cal.}$$

$$Th(OH)_4 = Th^{+4} + 4OH^-, \qquad K = \text{ca } 10^{-50}$$

The approximate value for the free energy of thoric ion is ca −197,100 cal.

$$Th = Th^{+4} + 4e^-, \qquad E° = \text{ca } 2.06$$

Even if this value for the free energy is approximately correct, it will not be useful without the data on the activity coefficients and hydrolysis constants for the ion, which are entirely lacking at present.

Since the oxide is not soluble in hydroxide, we may write, for the Th—ThO_2 couple in alkaline solution,

$$4OH^- + Th = ThO_2 + 2H_2O + 4e^-, \qquad E_B° = 2.64$$

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[7] Pissarjewsky, L., Z. anorg. allgem. Chem., **25**, 394 (1900).

Summary of group potentials. The titanium potentials were summarized at the end of the discussion of that element. For comparison, the overall potentials from the metals to the +4 state in acid solution are given below.

$$\mathrm{Ti} \overset{\text{ca } 0.95}{\text{——————}} \mathrm{TiO^{++}}$$

$$\mathrm{Zr} \overset{1.53}{\text{——————}} \mathrm{ZrO^{++}}$$

$$\mathrm{Hf} \overset{1.68}{\text{——————}} \mathrm{HfO^{++}}$$

$$\mathrm{Th} \overset{\text{ca } 2.06}{\text{——————}} \mathrm{Th^{+4}}$$

CHAPTER XIX

Boron, Aluminum, Scandium, Yttrium, Lanthanum, Rare Earth Elements, and Actinium

This group of elements has three valence electrons. In the monatomic gaseous atoms of boron and aluminum the ground state of these electrons is $s^2p^1(^2P_{1/2})$ while in the other members of the group it is $s^2d^1(^2D_{3/2})$, with the exception that the electronic states of the rare earths are further complicated by the presence of electrons in the low lying $4f$ level. Although these f electrons are not generally involved in compound formation, they do interact with the s^2d^1 electrons to produce complicated electronic states in the gas atoms. A complete interpretation of these spectra has not yet been given.

The reason for considering these elements as a group is that their chemistry, with the exception of boron, is essentially the chemistry of the +3 ions and these ions are all of the "octet" type, save for complication in the rare earths, introduced by the incomplete $4f$ electronic level, as noted above. The elements of the group are highly electropositive, and practically no free energies have been obtained by direct equilibrium measurements involving the elements. Thermal data are also very meager and permit of few accurate third-law calculations.

Boron

The preparation of pure solid boron is difficult, and most of the older preparations were an amorphous form containing some oxide or metallic borides. Pure crystalline boron has been prepared.[1] This should be taken as the standard state but the thermal data appear to refer to the amorphous form and the difference in energy between the two is unknown. Bichowsky and Rossini have estimated 115 kcal. as the heat of sublimation. The entropy of the gas is 36.7 cal. per degree and that of the solid probably about 1.5; hence the ΔS° of sublimation is around 35.2 units.

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[1] Cf. Kahlenberg, H. H., Trans. Am. Electrochem. Soc., 47, 56 (1925).

Oxidation states. The oxide, BO, is known as an unstable gas molecule from spectroscopic data, and the suboxides B_7O and B_3O have been reported. However, there is no definite proof that these substances are not small amounts of B_2O_3 in amorphous boron. A number of boron hydrogen compounds, for example, B_2H_6, B_4H_{10}, B_5H_9, are well known. No oxidation numbers will be assigned the boron in these compounds. The bonds are definitely nonpolar, but there are not enough electrons to give electron-pair bonds. Their structure has been discussed by Pauling.[2]

The important oxidation state is +3 and the oxide, B_2O_3, is the anhydride of the weak boric acids which are discussed below in some detail. The oxide has slight basic properties. The trihalides form at high temperatures, but all except the fluoride hydrolyze completely in water with the formation of boric acid. The fluoride forms complex ions, for example, BF_4^-. The sulfide, B_2S, is also completely hydrolyzed in water.

Boric acids and their salts. The solid acid, H_3BO_3, is somewhat soluble in cold water and quite soluble in hot. The solubility at 25° C. is 0.933 moles per 1000 g H_2O. Salts of the ortho-acid, H_3BO_3, may be formed by fusing the acid with alkalies, but in water the ortho-ion is hydrolyzed,

$$BO_3^{---} + 2H_2O = H_2BO_3^- + 2OH^-.$$

In solution one cannot distinguish between the dihydrogen ortho-ion, $H_2BO_3^-$, and the meta-ion, BO_2^-. Salts of the latter readily crystallize from water solution, but the formula $H_2BO_3^-$ will be used. At low concentrations of boric acid the molecular species is H_3BO_3 or HBO_2. The ionization constant of this acid has been determined by a number of investigators but we shall use the value of Owens:[3]

$$H_3BO_3 = H_2BO_3^- + H^+, \qquad K = 5.8 \times 10^{-10}.$$

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[2] Pauling, L., J. Am. Chem. Soc., **53**, 3225 (1931).

[3] Owens, B. B., J. Am. Chem. Soc., **56**, 1695 (1934).

At high concentrations the acid polymerises with the formation of tetraboric acid, $H_2B_4O_7$, and possibly more complicated polyacids. This acid is considerably stronger than the ortho-acid.

Kolthoff[4] has studied the concentration of hydrogen ion in these solutions. Assuming that the ionization,

$$H_2B_4O_7 = H^+ + HB_4O_7^-$$

is much greater than that of the ortho-acid, he has shown that at concentrations above 0.5 molal

$$\frac{(H^+)^2}{(H_3BO_3)^4} = K = 9.7 \times 10^{-8} \text{ at } 18° \text{ C.}$$

Metaborates in dilute solution hydrolyze in a normal manner with the formation of the acid H_3BO_3 and hydroxide in agreement with the value for the acid constant given above. However, the tetraborate ion decomposes according to the equation

$$B_4O_7^{--} + 5H_2O = 2H_3BO_3 + 2H_2BO_3^-, \qquad K = \text{ca } 10^{-3}$$

The value of the constant is taken from some unpublished calculations by Bray[5] on distribution ratio experiments with borate and boric acid solutions by Mueller and Abegg.[6] Hence, at concentrations of tetraborate below 0.1 *M*, the ion is largely decomposed and the alkalinity is determined by the hydrolysis of the $H_2BO_3^-$ ion. The constant for the complex formation in alkaline solution could be compared with the constant found by Kolthoff in acid solution if the second dissociation constant of the tetraboric acid were known.[7] The value,

$$HB_4O_7^- = H^+ + B_4O_7^{--}, \qquad K = \text{ca } 10^{-9}$$

would appear to bring the two into reasonable agreement. The constant for the first step of the dissociation is not determined by this calculation but by analogy with the general ratio of the first and second constants. One estimates

$$H_2B_4O_7 = H^+ + HB_4O_7^-, \qquad K = \text{ca } 10^{-4}.$$

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[4] Kolthoff, I. M., Rec. trav chim., **45**, 501 (1926).

[5] Bray, W. C., unpublished material (University of California, 1928).

[6] Mueller, P., and Abegg, R., Z. physik. Chem., **57**, 513 (1906).

[7] The author is indebted to Professor W. C. Bray for this observation.

It may also be pointed out that, since the dissociation of the tetraborate ion gives approximately equal concentrations of H_3BO_3 and $H_2BO_3^-$, the hydrogen ion concentration in tetraborate solutions is equal to K for H_3BO_3.

$$(H^+) = \frac{K(H_3BO_3)}{H_2BO_3^-} = K(\text{when } H_3BO_3 = H_2BO_3^-)$$

Boron potentials. All heats of formation of boron compounds depend, for their absolute value, upon the heat of formation of boron trichloride. This measurement of the direct union of boron and chlorine is probably not of high accuracy. However, the heats will be used to calculate a few boron potentials which are at least of the right order of magnitude.

From the heat of formation of solid boric acid, H_3BO_3, ΔH°, $-251{,}600$ cal., and the estimated entropy of the substance, 18 cal. per degree, one computes ΔS°, -104 cal. per degree and ΔF°, $-220{,}600$ cal. Within the accuracy of this value, the free energy of solution of the acid is zero; hence the same free energy will be used for the acid in solution.

$$3H_2O + B = H_3BO_3 + 3H^+ + 3e^-, \qquad E^\circ = 0.73$$

In view of this comparatively small potential for the reduction of boron, it is odd that the element cannot be obtained by reduction in water solutions. Its behavior in this respect is similar to carbon. Amorphous boron has been prepared by the cathodic reduction of the fused oxide and halides or of mixtures of the two, but the process is not a satisfactory one.

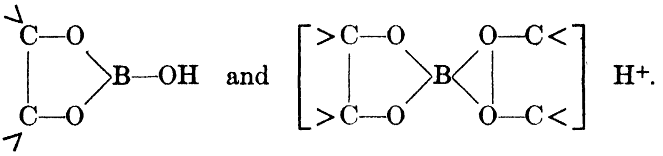
From the dissociation constant of the acid, one calculates for the free energy of ionization, 12,600 cal., and for the free energy of formation of the ion, $H_2BO_3^-$, ca $-208{,}000$ cal. The potential in alkaline solution then is,

$$4OH^- + B = H_2BO_3^- + 2H_2O + 3e^-, \qquad E_B^\circ = 2.5.$$

The heat of formation of the fluoborate, BF_4^-, is given as $-358{,}000$ cal. An estimate of the entropy of the ion as 40 gives, as a rough value for the free energy of formation, $-335{,}900$ cal. The corresponding potential is,

$$4F^- + B = BF_4^- + 3e^-, \qquad E^\circ = 1.06.$$

Heteroboric acids. The polyalcohols, especially those with hydroxyl groups on adjacent carbon atoms, combine with boric acid to form hetero-acids of the types



With the more complicated alcohols, such as mannitol, two or three molecules of boric acid may react with one of the alcohol.

Kolthoff[8] studied the complex with glycerine and gave the following equilibrium constants:

$$H_3BO_3 + \text{glycerine} = H_3BO_3 \cdot \text{glycerine}, \qquad K = 0.9$$

$$H_3BO_3 \cdot \text{glycerine} = H^+ + A^-, \qquad K = 3 \times 10^{-7}.$$

Advantage has been taken of the increased strengths of the heteroboric acids in the standard volumetric titration of boric acid with alkali.

Yabroff, Branch, and Bettman[9] have determined the ionization constants of a number of hydrocarbon boric acids and have discussed their results in terms of the resonance and negativity of the various groups. They gave the following constants:

PHENYLBORIC ACID,	$K = 137 \times 10^{-10}$
o-TOLYLBORIC ACID,	$K = 18.1 \times 10^{-10}$
BENZYLBORIC ACID,	$K = 75.5 \times 10^{-10}$
β-PHENYLETHYLBORIC ACID,	$K = 10.0 \times 10^{-10}$
n-BUTYLBORIC ACID,	$K = 1.82 \times 10^{-10}$

Aluminum

The standard state of aluminum is the solid metal. Kelley[10] has given the following data for the sublimation of the metal: $\Delta H°$, 67,497 cal.; $\Delta S°$, 32.58 cal. per degree; $\Delta F°$, 57,785 cal.

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[8] Kolthoff, I. M., Rec. trav. chim., **44**, 975 (1925).

[9] Yabroff, D. L., Branch, G. E. K., and Bettman, B., J. Am. Chem. Soc., **56**, 1852 (1934).

[10] Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).

Oxidation states. The only stable oxidation state is that of +3 aluminum. The hydroxide is amphoteric; with acids it forms compounds of the ion, Al^{+++}, and with bases salts of the metaluminate ion, AlO_2^-, and a few salts of orthoaluminate and polyaluminate ions. The fluoride is acidic, and many fluoaluminates are known. Aluminum sulfide and carbonate are completely hydrolyzed. The phosphate is but slightly soluble.

Aluminum potentials. Numerous attempts have been made to measure the potential of the aluminum electrode. The best results have been obtained with aluminum amalgam but the potentials, at least in acid solution, have not been reproducible. Latimer and Greensfelder[11] determined the entropy of cesium alum and aluminum ion. A recalculation of the entropy of the latter, using our present entropy data, gives −76 cal. per degree. It has not yet been definitely established that the correct entropy of hydrates can be obtained without carrying the specific heat measurements to temperatures below the boiling point of liquid helium. However, the error at most is not large. Using the Bichowsky and Rossini heat of formation of aluminum ion, that is, the heat of solution of aluminum in acid, ΔH°, −126,300 cal., and the entropy of the reaction, −36.0 cal. per degree, the ΔF° is −115,500 cal. The potential of the Al—Al^{+++} couple then is,

$$Al = Al^{+++} + 3e^-, \qquad E^\circ = 1.67.$$

For the third-law calculation of the free energy of aluminum hydroxide, we shall use the following data: entropy of the hydroxide, 20 cal. per degree (estimated); ΔH°, −304,900 cal.; ΔS°, −107.1 cal. per degree. The ΔF° of formation then is −272.900 cal. and the potential of the Al—$Al(OH)_3$ couple,

$$3OH^- + Al = Al(OH)_3 + 3e^-, \qquad E^\circ_B = 2.31.$$

The E°_B is, of course, without chemical significance as the hydroxide is soluble in 1 M OH^- with the formation of aluminate. Heyrovsky[12] reported for the aluminum amalgam electrode,

$$Al + 3H_2O = Al(OH)_3 + \tfrac{3}{2}H_2, \qquad E^\circ = 1.337$$

This would correspond to 2.17 for the above couple.

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[11] Latimer, W. M., and Greensfelder, B. S., J. Am. Chem. Soc., **50**, 2202 (1908).

[12] Heyrovsky, J., J. Chem. Soc., **117**, 27 (1920).

From our free energies we compute,

$$Al(OH)_3 = Al^{+++} + 3OH^-, \qquad K = 1.9 \times 10^{-33}$$

Heyrovsky[13] gave 1.06×10^{-33} and the K of chromic hydroxide is about 10^{-31}.

For the hydrolysis of aluminum ion, Bjerrum[14] reported,

$$Al^{+++} + H_2O = Al(OH)^{++} + H^+, \qquad K = 1.4 \times 10^{-5}.$$

This value should be recalculated, using activities. The problem appears to be complicated by the presence of appreciable concentrations of the ion $Al(OH)_2^+$ from the second step of the hydrolysis.

Various investigators[15] have given values of the acid dissociation constant of aluminic acid varying from 6×10^{-12} to 1.3×10^{-14}. We shall write

$$Al(OH)_3 = H^+ + H_2AlO_3^- \text{ (or } AlO_2^- + H_2O\text{)},$$

$$K = 4 \times 10^{-13}$$

The free energy of the aluminate ion, $H_2AlO_3^-$, then is −256,000 cal. and the potential of the Al—$H_2AlO_3^-$ couple,

$$4OH^- + Al = H_2AlO_3^- + H_2O + 3e^-, \qquad E^\circ_B = 2.35.$$

An approximate free energy of formation for the fluoaluminate ion is obtained from the following data: ΔH°, −542,000 cal.; ΔS° (estimated), −164 cal. per degree; ΔF°, −542,000 cal.

$$6F^- + Al = AlF_6^{---} + 3e^-, \qquad E^\circ = 2.13$$

$$AlF_6^{---} = Al^{+++} + 6F^-, \qquad K = 2.2 \times 10^{-24}.$$

In view of the large errors which may be involved in the thermal data, this constant is to be considered as giving merely the order of magnitude of the dissociation.

Scandium

The standard state of scandium is the metal. There are no data on the vapor pressure or the heat of sublimation. Bichowsky and Rossini have estimated 70,000 cal. for the latter.

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[13] *Ibid.*, 20.

[14] Bjerrum, N., Z. physik. Chem., **59**, 350 (1907).

[15] Maffei, A., Gazz. chim. ital., **64**, 149 (1934); Fricke, R., Koll. Z., **49**, 241 (1929); Kolthoff, I. M., Z. anorg. allgem. Chem., **112**, 185 (1920).

Oxidation states. The chemistry of scandium is concerned only with the +3 oxidation state. The hydroxide is more basic than is aluminum hydroxide. Unstable scandiumates such as $K_2Sc(OH)_5 \cdot 4H_2O$ have been prepared but they decompose to give the hydroxide when washed with water. The fluoride is but slightly soluble but dissolves in ammonium fluoride with the formation of the complex fluoride, ScF_4^-. The oxalate, phosphate, and carbonate are also but slightly soluble.

Scandium potentials. No thermal data are available. Bichowsky and Rossini estimate −410,000 cal. for the heat of formation of the oxide, from which we estimate

$$Sc = Sc^{+++} + 3e^-, \qquad E^\circ = \text{ca } 2.0.$$

Likewise there are no data on the solubility product of the hydroxide. As an estimate we give,

$$Sc(OH)_3 = Sc^{+++} + 3OH^-, \qquad K = \text{ca } 10^{-28}$$

Yttrium

The standard state is the metal. The heat of sublimation has been estimated as 90,000 cal. by Bichowsky and Rossini.

Oxidation states. The only oxidation state is the +3. The hydroxide has no acid properties and the same is true of the fluoride. The phosphate, carbonate, and oxalate are but slightly soluble in water, but the latter two dissolve in excess of the negative ion.

Yttrium potentials. No heats of formation of yttrium compounds have been determined. By comparison with aluminum and lanthanum the following estimates are given:

$$Y = Y^{+++} + 3e^-, \qquad E^\circ = \text{ca } 2.1$$

$$Y(OH)_3 = Y^{+++} + 3OH^-, \qquad K = \text{ca } 10^{-24}$$

The radius of yttrium ion is 0.82 Å and this value is similar to that of Dy^{+++} and Ho^{+++}. It is, therefore, to be expected that the basic character of yttrium hydroxide would be similar to that of the dysprosium and holmium hydroxides.

Lanthanum and the Rare Earth Elements

The standard state of these elements is the crystalline solid. However two crystalline modifications have been reported for lanthanum, cerium and praseodymium, and it is not possible to state which form has the lower energy. Klemm and Bommer[16] have found that the molecular volumes of europium and ytterbium, as metals, are much larger than those of the other rare earth elements and correspond closely to the values of Group II, alkaline earth metals. In view of the strong tendency of these elements to form compounds of the +2 oxidation state, these authors suggest that these two elements may be essentially divalent in the metallic state. There are no experimental values for the vapor pressures or heats of vaporization.

Oxidation states. Lanthanum readily loses its 1 *d* and 2 *s* electrons to form the +3 ion which has the electron structure of the noble gas, xenon. The rare earth elements similarly form the +3 ions, which also have the external structure of xenon but which differ, of course, in the 1 to 14 electrons in the 4*f* level. Of these various +3 ions, lanthanum with no *f* electrons, gadolinium with 7*f* electrons (that is, one in each *f* eigenfunction), and lutecium with 14*f* electrons are in *S* states and apparently are the most stable. These facts serve to account for the anomalous oxidation states and the so-called periodicity within the rare earth group. Thus, cerium, following lanthanum, tends to revert to the latter structure by losing 4 electrons to give a +4 oxidation state. Similar behavior is shown by terbium, following gadolinium. On the other hand, europium and ytterbium, preceding gadolinium and lutecium, respectively, also tend to form the *S* state structure of the two latter ions and thus show +2 oxidation states. Continuing this line of reasoning, one would expect praseodymium and dysprosium to have +5 as their maximum oxidation states. Prandtl and Huttner[17] have shown that the oxidation product of praseodymium is Pr_6O_{11} which they considered to be the praseodymium praseodymate, $2Pr_2O_3 \cdot Pr_2O_5$, but the oxide may be a mixture of Pr_2O_3 and PrO_2, as the latter oxide has been prepared in practically pure form. There is no evidence of higher oxidation states in dysprosium. Neodymium forms the dioxide.

Samarium and thulium might be expected to form +1 compounds, but so far none have been prepared. However samarium, definitely, and thulium, probably, form compounds of the +2 oxidation state.

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[16] Klemm, W., and Bommer, H., Z. anorg. allgem. Chem., **231**, 154 (1937).

[17] Prandtl, W., and Huttner, K., Z. anorg. allgem. Chem., **136**, 289 (1924).

Properties of the +3 state. The heats of formation of the +3 ion have been determined for lanthanum, cerium, praseodymium, and neodymium. The values are similar. There probably is an appreciable variation of the heat with increasing atomic number. Some periodicity within the group may exist, but no definite predictions may be made. The entropies of the ions have not been obtained; however, the value for lanthanum is probably around −40 units and that for lutecium 5 to 10 units less. Using this estimate for lanthanum ion, and the heat of formation, −165,900 cal., one calculates for the free energy of formation, −163,800 cal., and for the La—La^{+++} couple,

$$La = La^{+++} + 3e^-, \qquad E^\circ = 2.37.$$

Sadolin[18] reported for the solubility product of lanthanum hydroxide, 1.2×10^{-19} when freshly precipitated and 1.05×10^{-21} upon aging for some time. We shall write,

$$La(OH)_3 = La^{+++} + 3OH^-, \qquad K = \text{ca } 10^{-20}.$$

The corresponding free energy of the hydroxide is ca −303,800 cal. and the potential of the couple in alkaline solution,

$$3OH^- + La = La(OH)_3 + 3e^-, \qquad E^\circ_B = 2.76$$

The ionic radii decrease from 1.0 Å. for La^{+++} to 0.93 Å. for Ce^{+++} and then decrease quite regularly to 0.78 Å. for Lu^{+++}. The solubility products doubtless show the same trend.[19] We estimate,

$$Lu(OH)_3 = Lu^{+++} + 3OH^-, \qquad K = \text{ca } 10^{-26}.$$

Rimbach and Schubert[20] gave the following solubility products for cerium oxalate and tartrate:

$$Ce_2(C_2O_4)_3 \cdot 10H_2O = 2Ce^{+++} + 3C_2O_4^{--} + 10H_2O,$$
$$K = 2.5 \times 10^{-29}$$

$$Ce_2(C_4H_4O_6)_3 \cdot 9H_2O = 2Ce^{+++} + 3C_4H_4O_6^{--} + 9H_2O,$$
$$K = 9.7 \times 10^{-20}.$$

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[18] Sadolin, E., Z. anorg. allgem. Chem., **160**, 143 and 150 (1927).

[19] Cf. Endres, G., Z. anorg. allgem. Chem., **205**, 321 (1932).

[20] Rimbach, E., and Schubert, A., Z. physik. Chem., **67**, 198 (1909).

The constants are based upon concentrations and not activities. The same authors reported similar values for the oxalates of praseodymium, neodymium, and samarium. For ytterbium oxalate their constant is,

$$Yb_2(C_2O_4)_3 \cdot 10H_2O = 2Yb^{+++} + 3C_2O_4^{--} + 10H_2O, \qquad K = 4.4 \times 10^{-25}.$$

These authors reported the solubility of cerium iodate, $Ce(IO_3)_3 \cdot 2H_2O$ as 0.0074 *M* and lanthanum iodate, $2La(IO_3)_3 \cdot 3H_2O$, as 0.0085 *M*.

The oxalates are not appreciably soluble in hydrogen ion but tend to form complex oxalate ions with excess oxalate, especially in the case of the heavier rare earths.

The fluorides are but slightly soluble and do not dissolve in ammonium fluoride. The phosphates and carbonates are also insoluble but the heavier carbonates dissolve in ammonium carbonate with complex ion formation.

The dioxides. Cerium dioxide is a well-defined compound. Praseodymium, neodymium, and terbium form oxides in which their oxidation number is greater than +3. However, the preparation of the pure dioxide is difficult. Cerium dioxide, when hydrated, dissolves readily in sulfuric acid, but the other dioxides evolve oxygen in acid solution.

Ceric sulfate has become a valuable volumetric reagent.[21] Its use in analysis closely parallels that of permanganate. Kunz[22] studied the potential of the Ce^{+3}—Ce^{+4} couple against the hydrogen couple in sulfuric acid. In one *M* acid and equal concentration of the two ions, he reported,

$$(\text{In } 1M\ H_2SO_4)\ Ce^{+3} = Ce^{+4} + e^-, \qquad E = -1.44.$$

Noyes and Garner[23] studied the potential in nitric acid solution. They found that the potential varied but little on changing the concentration of nitric acid between 0.5 and 2 *M*, indicating little tendency toward complex nitrate formation. They wrote, without correcting for the difference in the activities of the +3 and +4 ions,

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[21] Willard, H. H., and Young, P., J. Am. Chem. Soc., **50**, 1322 (1928); Furman, N. H., J. Am. Chem. Soc., **50**, 755 (1928).

[22] Kunz, A. H., J. Am. Chem. Soc., **53**, 98 (1931).

[23] Noyes, A. A., and Garner, C. S., J. Am. Chem. Soc., **58**, 1265 (1936).

$$Ce^{+3} = Ce^{+4} + e^-, \qquad E^\circ = -1.61.$$

On the basis of this value it would seem that the sulfate solution investigated by Kunz must be subject to considerable complex formation.

The potentials of the other rare earth +4 ions must be considerably more negative, in view of their rapid decomposition of water.

$$Pr^{+3} = Pr^{+4} + e^-, \qquad E^\circ < -1.6.$$

Properties of the +2 ions. Europous ion is stable in water solutions, at low hydrogen-ion concentrations, and the slightly soluble ytterbous and samarous sulfates are not rapidly oxidized by water. These elements also form +2 halides by reduction of the +3 compounds by hydrogen at high temperatures.

McCoy[24] prepared europous solutions by reduction with zinc. He gave for the Eu^{++}—Eu^{+++} couple

$$Eu^{++} = Eu^{+++} + e^-, \qquad E^\circ = 0.43.$$

From their chemical behavior we estimate,

$$Yb^{++} = Yb^{+++} + e^-, \qquad E^\circ = \text{ca } 0.6$$

$$Sm^{++} = Sm^{+++} + e^-, \qquad E^\circ = \text{ca } 0.8.$$

In their solubilities, the compounds of the +2 rare earth ions appear to be similar to the corresponding barium compounds.

Actinium

The instability of the actinium nucleus precludes the accumulation of any appreciable quantity of the element, the half-life of the element being only about 20 years and the abundance of its parent element, proactinium, being also very low. The chemical properties of actinium compounds resemble those of the rare earths, especially lanthanum. The metal must be highly electropositive. The hydroxide is somewhat soluble in ammonium ion,[25] which agrees with the expectation that the hydroxide is more basic than is lanthanum hydroxide.

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[24] McCoy, H. N., J. Am. Chem. Soc., **58**, 1579 (1936).

[25] Cf. Hull, D. E., Libby, W. F., and Latimer, W. M., J. Am. Chem. Soc., **57**, 1649 (1935).

CHAPTER XX

Beryllium, Magnesium, Calcium, Strontium, Barium, and Radium

The elements of this group have two valence electrons and, in the monatomic gas atoms, the ground state is $s^2(^1S_0)$. The elements are highly electropositive and the only oxidation state, stable in water solutions, is the +2. The electronic structure of the ions is that of the preceding noble gas. Because of the small ionic radius, the oxide of beryllium is amphoteric, but with increasing size of the heavier members of the group, the oxides become strong bases.

Beryllium

The standard thermodynamic state of beryllium is the solid metal. The entropy of sublimation is 30.2 cal. per degree but there are no experimental data on the heat or free energy of sublimation. Bichowsky and Rossini estimate 75,000 cal. for the former.

Oxidation states. Spectroscopic data have been obtained on the unstable +1 fluoride, BeF; however, only the +2 state has chemical significance. As stated above, the oxide or hydroxide is amphoteric. The hydroxide and phosphate are only slightly soluble, but the normal salts of most of the acid ions are soluble. However insoluble basic salts form at low acid concentration. The basic carbonate is soluble in excess carbonate ion, and the fluoberyllate, BeF_4^{--}, forms at high fluoride concentration.

Beryllium free energies. Bichowsky and Rossini gave −85,000 cal. as the heat of formation of the ion, Be^{++}. From an extrapolation of the entropies of the other members of the group against their atomic radii, we estimate −50 cal. per degree as the entropy of the ion. One then computes for the solution of beryllium in acid, $\Delta S°$, −21.1, and $\Delta F°$, −78,700 cal. The latter figure is also the free energy of formation of the ion. For the Be—Be^{++} couple, one then finds

$$Be = Be^{++} + 2e^-, \qquad E° = 1.70$$

Bodforss[1] and others have sought to measure the beryllium potential by direct cell measurements. The value obtained is around 0.6. The electrode is obviously highly polarized.

Various investigators have agreed that the freshly precipitated hydroxide has the formula $Be_2O(OH)_2$. This form, however, is metastable and two modifications with the formula $Be(OH)_2$ are claimed. Prytz[2] gave slightly different data for the hydrolysis of various halide solutions, but the following are representative:

$$2Be^{++} + H_2O = Be_2O^{++} + 2H^+, \qquad K = 4 \times 10^{-7}$$

$$Be_2O(OH)_2 = Be_2O^{++} + 2OH^-, \qquad K = 4 \times 10^{-19}$$

$$Be_2O(OH)_2 + H_2O = 2Be^{++} + 4OH^-, \qquad K = 1 \times 10^{-40}$$

The calculated free energy of the hydroxide, $Be_2O(OH)_2$, then is $-305{,}610$ cal.

For the equilibrium constant of the solid and its acid ions, Bleyer and Kaufmann[3] reported,

$$H_2Be_2O_3(s) = 2H^+ + Be_2O_3^{--}, \qquad K = 7.3 \times 10^{-30}.$$

These authors also gave,

$$H_2BeO_2(I) = 2H^+ + BeO_2^{--}, \qquad K = 2.8 \times 10^{-30}.$$

$$H_2BeO_2(II) = 2H^+ + BeO_2^{--}, \qquad K = 1.4 \times 10^{-30}.$$

One then calculates for the free energy of the diberyllate ion, $Be_2O_3^{--}$, $-265{,}810$ cal., and for the couple in alkaline solution,

$$6OH^- + 2Be = Be_2O_3^{--} + 3H_2O + 4e^-, \quad E_B^\circ = 2.28.$$

We can give no data on the equilibrium between $Be_2O_3^{--}$ and BeO_2^{--} in the alkaline beryllate solutions. When the solutions are heated, the H_2BeO_2 form of the acid is said to be precipitated, but the data are insufficient for the calculation of its free energy.

No values can be given for the solubility products of the phosphate or the numerous basic salts of other negative ions.

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[1] Bodforss, S., Z. physik. Chem., **124,** 66 (1926); *ibid.*, **130,** 85 (1927). Cf. also Neumann, B., and Richter, H., Z. Elektrochem., **31,** 296 (1925).

[2] Prytz, M., Z. anorg. allgem. Chem., **197,** 111 (1931).

[3] Bleyer, B., and Kaufmann, S. W., Z. anorg. Chem., **82,** 83 (1913).

Magnesium

The standard state of magnesium is the metal. For the sublimation to give the monatomic gas, Kelley[4] gave ΔH°, 35,907 cal., ΔF°, 27,640 cal.

Oxidation states. Although the +2 oxidation state is the only one of importance, claims are made for the formation of compounds of the +1 state by high temperature reduction. The probable free energies will be discussed. The +2 hydroxide is distinctly basic. The hydroxide, carbonate fluoride, and ammonium phosphate are the more important slightly soluble compounds.

Free energy of Mg^{++} and its compounds. For the free energy of formation of magnesium ion, that is, the free energy of solution of magnesium in hydrogen ion, we find: ΔH°, $-110{,}230$ cal.; ΔS°, -8.2 cal. per degree; and ΔF°, $-107{,}780$ cal. The potential of the Mg—Mg^{++} couple is,

$$Mg = Mg^{++} + 2e^-, \qquad E^\circ = 2.34.$$

This value is to be preferred to the older value by Latimer[5] which was calculated from less accurate thermal data.

We shall use the data of Kline[6] for the solubility product of magnesium hydroxide,

$$Mg(OH)_2 = Mg^{++} + 2OH^-, \qquad K = 5.5 \times 10^{-12}.$$

The free energy of formation of the solid hydroxide then is $-193{,}300$ cal., and the potential for the Mg—$Mg(OH)_2$ couple,

$$2OH^- + Mg = Mg(OH)_2 + 2e^-, \qquad E_B^\circ = 2.67.$$

Kelley and Anderson[7] have given ΔF° for MgO as $-136{,}370$ cal. and ΔF° for $MgCO_3$ as $-246{,}630$ cal. Combining the latter with our values for the free energies of magnesium and carbonate ions would give about 10^{-9} for the solubility product of magnesium carbonate. This probably is too small. However, it is a fairly good check on the free energies, as these values were obtained from high temperature equilibria. Kline[8] reported

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[4] Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).

[5] Latimer, W. M., J. Phys. Chem., **31**, 1267 (1927).

[6] Kline, W. D., J. Am. Chem. Soc., **51**, 2096 (1929).

[7] Kelley, K. K., and Anderson, C. T., U. S. Bur. Mines Bull., No. 384 (1935).

$$MgCO_3 \cdot 3H_2O = Mg^{++} + CO_3^{--} + 3H_2O, \quad K = \text{ca } 1 \times 10^{-5}$$

The solubility of magnesium ammonium phosphate was studied by Bube.[9] He found

$$Mg(NH_4)PO_4 = Mg^{++} + NH_4^{+} + PO_4^{---}, \quad K = 2.5 \times 10^{-13}$$

Kohlrausch,[10] from conductivity measurements, has recorded the following solubility products:

$$MgF_2 = Mg^{++} + 2F^{-}, \quad K = 6.4 \times 10^{-9}$$

$$MgC_2O_4 = Mg^{++} + C_2O_4^{--}, \quad K = 8.6 \times 10^{-5}$$

The free energy of Mg^{+}. It is claimed that the reduction of the magnesium dihalides at high temperatures results in the formation of the monohalides.

Grimm and Herzfeld[11] employed a Born-Haber cycle to calculate the free energy of formation of the monohalides. A recalculation of their cycle using our present data gives −29.3 kcal. for the heat of formation of MgCl and, except for any error involved in the assumption that MgCl has the same lattice energy as NaCl, the calculated heat should be correct to at least 5 kcal. Estimating the entropy of MgCl to be equal to that of sodium chloride, one calculates −24,000 cal. for the free energy of formation. A third-law calculation for $MgCl_2$ gives −143,000 cal. as its free energy. One then sees that the +1 chloride is very unstable with respect to the decomposition,

$$2MgCl = MgCl_2 + Mg, \quad \Delta F^\circ = -95{,}000 \text{ cal.}$$

Now the entropy of this reaction is so small that there will be no appreciable change in ΔF°, even at 1000°, and one may state definitely that either the subchloride is a mixture of the metal and the dichloride, or its lattice energy is far different from that of sodium chloride. The latter might be the case, as the ion, Mg^{+}, has 1 unpaired *s* electron and, like mercurous ion, will probably form the double ion, Mg_2^{++}, with an electron pair bond between the magnesium atoms. Additional evidence in favor of the subchloride is given by the work of Gomberg and Bachmann.[12] In order to explain the action of a magnesium and magnesium iodide mixture in the reduction of certain organic compounds, these investigators were led to assume the formation of MgI as an intermediate.

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[8] Kline, W. D., J. Am. Chem. Soc., **51**, 2093 (1929).

[9] Bube, K., Z. anal. Chem., **49**, 557 (1910).

[10] Kohlrausch, F., Z. physik. Chem., **64**, 164 (1908).

[11] Grimm, H. G., and Herzfeld, K. F., Z. Physik., **16**, 77 (1923).

However, the band spectra data on MgF(gas) lead to a heat of formation of 95 kcal., endothermic (Bichowsky and Rossini), which would definitely preclude the existence of the solid monofluoride. See also calcium in the +1 state.

Calcium

The standard state of calcium is the face-centered cubic form which is stable up to about 300° C. At least one and probably two other modifications exist at higher temperatures. For the process of sublimation, Kelley[13] has given the following data: ΔH°, 42,571 cal.; ΔF°, 34,508 cal.; and ΔS°, 27.05 cal. per degree.

Oxidation states. Like magnesium, highly unstable +1 halides may exist, but the only oxidation state stable in water solutions is the +2. The hydroxide is more basic than magnesium hydroxide and the solubilities of the sulfate and oxalate are much lower.

Calcium free energies. The free energy of calcium ion may be calculated from the following data for the solution of the metal in acid: ΔH°, $-129{,}740$ cal.; ΔS°, 9.9 cal. per degree; and ΔF°, $-132{,}700$ cal. For the potential of the Ca—Ca^{++} couple, one then computes,

$$Ca = Ca^{++} + 2e^-, \qquad E^\circ = 2.87.$$

Although the data are slightly different, the free energy and potential are the same as calculated previously by Latimer.[14] The best experimental value for this potential appears to be that of Tamele[15] who obtained 2.76, using an amalgam electrode.

For the free energy of solution of the hydroxide, we shall use the value 6960 cal.[16] The free energy of the hydroxide then is −214,830 cal. and the potential of the couple in alkaline solution,

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[12] Gomberg, M., and Bachmann, W. E., J. Am. Chem. Soc., **49**, 236 (1927).

[13] Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).

[14] Latimer, W. M., J. Phys. Chem., **31**, 1267 (1927).

[15] Tamele, M., J. Phys. Chem., **28**, 502 (1924).

$$2OH^- + Ca = Ca(OH)_2 + 2e^-, \qquad E_B^\circ = 3.02$$

The corresponding value for the solubility product is,

$$Ca(OH)_2 = Ca^{++} + 2OH^-, \qquad K = 7.9 \times 10^{-6}$$

The most reliable value for solubility product of calcium carbonate appears to be that of Frear and Johnston[17] who found

$$CaCO_3 = Ca^{++} + CO_3^{--}, \qquad K = 4.82 \times 10^{-9},$$
$$\Delta F^\circ = 11{,}340 \text{ cal.}$$

Combining this with our free energies of the ions, we obtain for the free energy of formation of calcium carbonate, −270,430 cal. This value is in fairly good agreement with that calculated from the heat (Bichowsky and Rossini) and entropy of formation of the carbonate: ΔH°, −289,500 cal.; ΔS°, 62.7 cal. per degree; ΔF°, −270,800 cal.

Kelley and Anderson[18] have calculated for the aragonite-calcite transition,

$$\underset{\text{(aragonite)}}{CaCO_3} = \underset{\text{(calcite)}}{CaCO_3} \qquad \Delta H^\circ = 42 \text{ cal.},$$
$$\Delta F^\circ = -273 \text{ cal.}$$

This free energy could be used to calculate the solubility product of aragonite.

For the free energy of solution of calcium sulfate, Latimer, Hicks, and Schutz[19] computed 6308 cal.

$$CaSO_4 \cdot 2H_2O = Ca^{++} + SO_4^{--} + 2H_2O, \qquad K = 2.4 \times 10^{-5}$$

The same authors[20] summarized the data on the solubility of calcium oxalate and chose for ΔF°, 11,791 cal.

$$CaC_2O_4 \cdot H_2O = Ca^{++} + C_2O_4^{--} + H_2O, \qquad K = 2.27 \times 10^{-9}$$

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[16] Cf. Latimer, W. M., Schutz, P. W., and Hicks, J. F. G., Jr., J. Am. Chem. Soc., **55**, 971 (1933).

[17] Frear, G. L., and Johnston, J., J. Am. Chem. Soc., **51**, 2082 (1929).

[18] Kelley, K. K., and Anderson, C. T., U. S. Bur. Mines Bull., No. 384 (1935).

[19] Latimer, W. M., Hicks, J. F. G., Jr., and Schutz, P. W., J. Chem. Phys., **1**, 620 (1933).

[20] Latimer, W. M., Schutz, P. W., and Hicks, J. F. G., Jr., J. Am. Chem. Soc., **55**, 974 (1933).

Britton[21] gave the following values for the calcium phosphates:

$$CaHPO_4 = Ca^{++} + HPO_4^{--}, \qquad K = \text{ca } 5 \times 10^{-6}$$

$$Ca_3(PO_4)_2 = 3Ca^{++} + 2PO_4^{--}, \qquad K = 1 \times 10^{-25}$$

From conductance measurements, Kohlrausch[22] reported,

$$CaF_2 = Ca^{++} + 2F^-, \qquad K = 3.9 \times 10^{-11}$$

The solubility of calcium iodate was studied by Kilde.[23] He has recorded,

$$Ca(IO_3)_2 \cdot 6H_2O = Ca^{++} + 2IO_3^- + 6H_2O, \qquad K = 1.93 \times 10^{-6}$$

Paul[24] gave for the solubility product of the tartrate,

$$CaC_4H_4O_6 \cdot 2H_2O = Ca^{++} + C_4H_4O_6^{--} + 2H_2O, \qquad K = 7.7 \times 10^{-7}.$$

The free energy of the hydride, CaH_2, is discussed under hydrogen and that of the peroxide, CaO_2, under oxygen.

Calcium in the +1 state. Guntz and Benoit[25] claim the formation of the subhalides by reduction with the metal at 1000°. It has been pointed out by Bichowsky and Rossini that their heat of solution of CaCl in acid is just the value which would be given by a mixture of the metal and the dichloride. The heat of formation of the subchloride from their work is −96.9 kcal. while the value calculated from a Born-Haber cycle is −40.3 kcal. and the corresponding free energies would be about −92 and −35 kcal. From band spectra data the heat of formation of the gaseous subfluoride, CaF, is 3 kcal. Estimating the heat of sublimation to be the same as that for potassium fluoride, 53 kcal., we find the heat of formation of the solid CaF to be −50 kcal. This value is in line with the Born-Haber cycle figure for CaCl, and would make the fluoride highly unstable.

$$2CaF(s) = Ca + CaF_2, \qquad \Delta H^\circ = \Delta F^\circ = -190 \text{ kcal.}$$

See also the discussion of +1 magnesium.

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[21] Britton, H. T. S., J. Chem. Soc., 614 (1927).
[22] Kohlrausch, F., Z. physik. Chem., **64**, 145 (1908).
[23] Kilde, G., Z. anorg. allgem. Chem., **218**, 115 (1934).
[24] Paul, T., Z. Elektrochem., **21**, 549 (1915).
[25] Guntz, A., and Benoit, F., Bull. soc. chim., **35**, 709 (1924).

Strontium

The standard thermodynamic state is the solid metal. Hartmann and Schneider[26] have given accurate data for the vapor pressure of the liquid.

$$\Delta F^\circ = 37{,}800 + 5.83\ T \log T - 44.58\ T.$$

There are no data on the solid, but we estimate: ΔH°, 38,500 cal.; ΔS°, 26.03 cal. per degree; ΔF°, 30,700 cal.

Oxidation states. The +1 halides are known as unstable gas molecules, and claims are made for the solids (cf. magnesium and calcium). The +2 hydroxide is more basic than is calcium, and the solubilities of the +2 sulfates and chromates are less than the calcium salts.

Strontium free energies. The free energy of the ion, Sr^{++}, may be calculated from the following data on the heat of solution of the metal in hydrogen ion: ΔH°, −130,040 cal.; ΔS°, 10.6 cal. per degree; ΔF°, −133,200 cal. From this free energy the potential of the Sr—Sr^{++} couple is

$$Sr = Sr^{++} + 2e^-, \qquad E^\circ = 2.89.$$

This potential is to be preferred to the older value by Latimer[27] which was 0.03 volts higher. Cell measurements using amalgam electrodes do not appear to be completely reversible.[28] The solubility of the octahydrated hydroxide, $Sr(OH)_2 \cdot 8H_2O$, is 0.086 M. Using 0.5 as a rough value for the activity coefficient, and neglecting the change in the activity of the water, we find the free energy of solution to be 4780 cal. and

$$Sr(OH)_2 \cdot 8H_2O = Sr^{++} + 2OH^- + 8H_2O, \qquad K = 3.2 \times 10^{-4}.$$

For the potential of the strontium couple in alkaline solution one then computes,

$$8H_2O + 2OH^- + Sr = Sr(OH)_2 \cdot 8H_2O + 2e^-, \qquad E_B^\circ = 2.99.$$

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[26] Hartmann, H., and Schneider, R., Z. anorg. allgem. Chem., **180**, 275 (1929).

[27] Latimer, W. M., J. Phys. Chem., **31**, 1267 (1927).

[28] Danner, P. S., J. Am. Chem. Soc., **46**, 2390 (1924).

McCoy and Smith[29] studied the solubility of strontium carbonate. From their work,

$$SrCO_3 = Sr^{++} + CO_3^{--}, \qquad K = 9.42 \times 10^{-10},$$

$$\Delta F^\circ = 12{,}310 \text{ cal.}$$

Our value for the free energy of formation of the carbonate, then, is $-271{,}900$ cal.

Randall[30] gave for strontium bicarbonate,

$$Sr(HCO_3)_2 = Sr^{++} + 2HCO_3^{-}, \qquad K = 1.83 \times 10^{-6},$$

$$\Delta F^\circ = 6314.$$

From conductivity measurements Kohlrausch[31] reported for 18° C.,

$$SrC_2O_4 \cdot H_2O = Sr^{++} + C_2O_4^{--} + H_2O, \qquad K = 5.61 \times 10^{-8}$$

$$SrSO_4(ppt) = Sr^{++} + SO_4^{--}, \qquad K = 2.8 \times 10^{-7}$$

$$SrF_2 = Sr^{++} + 2F^{-}, \qquad K = 3 \times 10^{-9}.$$

The solubility product of strontium chromate has been reported by Ruff and Ascher[32] as

$$SrCrO_4 = Sr^{++} + CrO_4^{--}, \qquad K = 3.6 \times 10^{-5}$$

Strontium iodate $Sr(IO_3)_2 \cdot 6H_2O$ and phosphate $Sr_3(PO_4)_2$ are but slightly soluble, but no data can be given.

Barium

The standard state of barium is the metal. Hartmann and Schneider[33] have studied the vapor pressure of liquid barium. The free energy may be represented by the equation,

$$\Delta F^\circ = 40{,}500 + 5.83\, T \log T - 40.32\, T.$$

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[29] McCoy, H. N., and Smith, H. J., J. Am. Chem. Soc., **33**, 468 (1911). Cf. Kelley, K. K., and Anderson, C. T., U. S. Bur. Mines Bull., No. 384 (1935).

[30] Randall, M., International Critical Tables, VII, 299.

[31] Kohlrausch, F., Z. physik. Chem., **64**, 152 and 168 (1908).

[32] Ruff, O., and Ascher, E., Z. anorg. allgem. Chem., **185**, 379 (1930).

[33] Hartmann, H., and Schneider, R., Z. anorg. allgem. Chem., **180**, 275 (1929). Cf. Kelley, K. K., U. S. Bur. Mines Bull., No. 283 (1935).

There are no data on the solid. The entropy of sublimation is roughly ΔS°, 25.6 cal. per degree.

Oxidation states. The existence of the molecule, BaCl, in barium flame spectra has been established. The solid subhalides are subject to the same doubts as expressed in the discussion of the similar compounds of calcium and magnesium. Marino[34] believed the product of the interaction of the metal and the dihalides to be a solid solution of the metal in the halide, and the energies of formation as calculated from Born-Haber cycles seem to bear out this contention. The +2 hydroxide is a fairly strong base. The solubilities of the sulfate and chromate are less than those of the lighter members of the group.

Barium free energies. The free energy of the ion, Ba^{++}, may be calculated from the following data on the solution of the metal in hydrogen ion: ΔH°, $-128{,}360$ cal.; ΔS°, 18.4 cal. per degree; ΔF°, $-133{,}850$ cal. The latter value is also the free energy of formation of the ion since the free energies of the other substances in the reaction are zero. One then calculates for the potential of the Ba—Ba^{++} couple,

$$\mathrm{Ba} = \mathrm{Ba}^{++} + 2e^-, \qquad E^\circ = 2.90$$

This value is the same as that previously calculated by Latimer.[35] Devoto[36] computed 2.96 from thermal data, and from the measurement of the decomposition potential of the molten chloride, obtained by extrapolation to 25°, he obtained 2.86. All the measurements in water solution with the amalgam electrode are much lower than the calculated reversible potential.

The free energy of solution of barium hydroxide has been given by Lewis and Randall,[37]

$$\mathrm{Ba(OH)_2 \cdot 8H_2O} = \mathrm{Ba}^{++} + 2\mathrm{OH}^- + 8\mathrm{H_2O},$$

$$\Delta F^\circ = 3140,$$

$$K = 5.0 \times 10^{-3}.$$

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[34] Marino, L., Atti. accad. Lincei, **24**, II, 148 (1915).

[35] Latimer, W. M., J. Phys. Chem., **31**, 1267 (1927).

[36] Devoto, G., Z. Elektrochem., **34**, 21 (1928).

[37] Lewis, G. N., and Randall, M., *Thermodynamics* (McGraw-Hill, New York, 1923), p. 490.

The free energy of the hydrated hydroxide is −665,680 cal. and the potential of the couple in alkaline solution,

$$8H_2O + 2OH^- + Ba = Ba(OH)_2 \cdot 8H_2O + 2e^-, \qquad E_B^\circ = 2.97.$$

From the investigation of McCoy and Smith,[38]

$$BaCO_3 = Ba^{++} + CO_3^{--}, \qquad K = 4.93 \times 10^{-9}, \qquad \Delta F^\circ = 11{,}330 \text{ cal.}$$

The free energy of formation of the carbonate is then computed to be −271,570 cal. Kelley and Anderson calculated −265,830 cal. from the heat and entropy of formation of the carbonate. However, the value for the heat of formation of the carbonate which they used is 6000 cal. less (negative) than that selected by Bichowsky and Rossini. This would appear to account almost entirely for the discrepancy.

For the free energy of solution of barium sulfate, Latimer, Hicks, and Schutz[39] calculated 13,718 cal. from data by Neumann.

$$BaSO_4 = Ba^{++} + SO_4^{--}, \qquad K = 9.9 \times 10^{-11}$$

The solubility of barium sulfate in sulfuric acid has been studied by Hammett and Deyrup.[40]

$$Ba(HSO_4)_2 = Ba^{++} + 2HSO_4^-, \qquad K = \text{ca } 2.7$$

Kohlrausch[41] has given the following data:

$$BaCrO_4 = Ba^{++} + CrO_4^{--}, \qquad K = 2 \times 10^{-10}$$

$$BaF_2 = Ba^{++} + 2F^-, \qquad K = 1.7 \times 10^{-6}$$

$$BaC_2O_4 \cdot 3\tfrac{1}{2}H_2O = Ba^{++} + C_2O_4^{--} + 3\tfrac{1}{2}H_2O, \qquad K = 1.62 \times 10^{-7}$$

$$BaC_2O_4 \cdot 2H_2O = Ba^{++} + C_2O_4^{--} + 2H_2O, \qquad K = 1.1 \times 10^{-7}$$

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[38] McCoy, H. N., and Smith, H. J., J. Am. Chem. Soc., **33**, 468 (1911). Cf. Kelley, K. K., and Anderson, C. T., U. S. Bur. Mines Bull., No. 384 (1935).

[39] Latimer, W. M., Hicks, J. F. G., Jr., and Schutz, P. W., J. Chem. Phys., **1**, 620 (1933).

[40] Hammett, L. P., and Deyrup, A. J., J. Am. Chem. Soc., **55**, 1908 (1933).

[41] Kohlrausch, F., Z. physik. Chem., **64**, 145 and 158 (1908).

From the work of Schlesinger and Siem,[42]

$BaMnO_4 = Ba^{++} + MnO_4^{--}$, $K = 2.5 \times 10^{-10}$.

Using the activity coefficient, 0.85, and the solubility of barium iodide, 7.9×10^{-4} *M*, given by Harkins and Winninghoff,[43] the solubility product of the iodate is,

$Ba(IO_3)_2 \cdot H_2O = Ba^{++} + 2IO_3^- + H_2O$, $K = 1.25 \times 10^{-9}$

The free energy of solution of barium bromate was given by Greensfelder and Latimer[44] as 7171 cal. The solubility product is,

$Ba(BrO_3)_2 \cdot H_2O = Ba^{++} + 2BrO_3^- + H_2O$, $K = 5.5 \times 10^{-6}$.

The solubilities of both the chloride and nitrate at 25° C. are not large. From the free energies of solution, −280 cal. and 3200 cal., respectively,[45] one calculates

$BaCl_2 \cdot 2H_2O = Ba^{++} + 2Cl^- + 2H_2O$, $K = 1.6$

$Ba(NO_3)_2 = Ba^{++} + 2NO_3^-$, $K = 4.5 \times 10^{-3}$.

Barium orthophosphate and the mono- and di-acid phosphates are but slightly soluble, but no quantitative data are available.

Barium peroxide and barium hydride are discussed under oxygen and hydrogen.

Radium

Radium metal has been prepared by first forming an amalgam by electrolysis of a radium chloride solution and then distilling off the mercury. It appears to be similar to barium in its properties. Judging from the trend in the group, the free energy of the ion and potential of the Ra—Ra^{++} couple are probably very close to the corresponding values for barium. Because of the greater size of the radium ion, it is to be expected that the hydroxide will be more basic. The solubility product for radium sulfate has been given by Nikitin and Tolmatscheff,[46]

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[42] Schlesinger, H. I., and Siem, H. B., J. Am. Chem. Soc., **46**, 1971 (1924). Cf. *Landolt-Bornstein Tabellen III*, p. 2134.

[43] Harkins, W. D., and Winninghoff, W. J., J. Am. Chem. Soc., **33**, 1827 (1911).

[44] Greensfelder, B. S., and Latimer, W. M., J. Am. Chem. Soc., **50**, 3289 (1928).

[45] Brown, O. L. I., Smith, W. V., and Latimer, W. M., J. Am. Chem. Soc., **58**, 1758 (1936); Latimer, W. M., and Ahlberg, J. E., Z. physik. Chem., **A148**, 464 (1930).

$$RaSO_4 = Ra^{++} + SO_4^{--}, \qquad K = 4.25 \times 10^{-11}$$

This value is just slightly less than that for barium sulfate. The chromate and nitrate are probably also less soluble than the corresponding barium salts.

Summary of group potentials. For ease in comparison, the following summary of the group potentials is given:

	$E°$
Be—Be^{++}	1.70
Mg—Mg^{++}	2.34
Ca—Ca^{++}	2.87
Sr—Sr^{++}	2.89
Ba—Ba^{++}	2.90

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[46] Nikitin, B., and Tolmatscheff, P., Z. physik. Chem., **A167**, 269 (1933).

CHAPTER XXI

Lithium, Sodium, Potassium, Rubidium, and Cesium

The elements of this group have but one valence electron and the state of the monatomic gas atoms is $s^1(^2S_{\frac{1}{2}})$. Because of the similarity and simplicity of the chemistry, the various thermodynamic properties will be discussed for the group as a whole.

The data in Table 31 for the sublimation of the elements has been summarized by Kelley.[1] At low concentrations of the metal vapors, the gases are monatomic, but at higher concentration appreciable formation of the diatomic molecules occurs. The heats of formation, entropies, and free energies of these diatomic molecules are known (cf. Bichowsky and Rossini and the entropy tables, Appendix V). The standard thermodynamic states of the elements are, of course, the solid metals.

Oxidation states. The only oxidation state is the +1. The so-called "subhalides" are obviously solid solutions or "colloidal solution" of the metals in the halides. Because of the low charge and large size of the +1 ions, the hydroxides are all soluble strong bases. The salts of the alkali metals with the common negative ions, with few exceptions, are readily soluble. In fact, salts with a solubility of less than 0.01 *M* are very rare.

The metal-metal ion potentials. Lewis and his co-workers[2] have measured the potentials of all the alkali ions except cesium against the alkali metal amalgam electrodes at such low concentrations of the metal that the decomposition of the water did not occur. They then measured the e.m.f. of the amalgam against the pure metal in nonaqueous solvents. These investigations were carried out with remarkable skill and ingenuity and their E° values for sodium and potassium are probably accurate to one-thousandth of a volt. However, the experimental difficulties in the case of lithium and rubidium were somewhat greater and these potentials are not in good agreement with those which we may calculate from thermal data. These calculations have been summarized in Table 32. The data refer, of course, to the solution of the metals in acid to form the ion and hydrogen gas. The agreement of the calculated and experimental E° for sodium and potassium, for which both the thermal data and e.m.f. measurements are most reliable, is satisfactory. At present we are unable to account for the discrepancies in the other two cases, especially in the case of lithium. The two most recent determinations of the heat of solution of the metal in water agree to 100 cal. and the error in the entropies would not appear to be greater than 350 cal., yet the deviation found is of the order of 2300 cal. For the free energies of formation of the ions, the following values in calories will be adopted: Li^+, −70,700; Na^+, −62,590; K^+, −67,430; Rb^+, −68,800; Cs^+, −70,280.

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[1] Kelley, K. K., U. S. Bur. Mines Bull., No. 383 (1935).

[2] Cf. Lewis, G. N., and Randall, M., *Thermodynamics* (McGraw-Hill, New York, 1923), p. 414.

TABLE 31

HEATS, ENTROPIES, AND FREE ENERGIES OF SUBLIMATION OF THE ALKALI METALS AT 298.15° K.

Element	ΔH°	ΔS°	ΔF°
Li	36,439	26.45	28,807
Na	25,949	24.52	18,639
K	21,521	23.10	14,637
Rb	20,505	24.00	13,352
Cs	18,828	22.13	12,231

Free energies of solution of alkali salts. Data will be given for the free energies of solution of the more common alkali metal compounds. This has not been done for the soluble salts of the other elements but the importance of these compounds would seem to warrant the inclusion of these data. If the solubility and activity coefficients for the saturated solutions are known, the free energy may be obtained by the ordinary thermodynamic methods. If the salt is a highly soluble hydrated compound, the activity of the water must also be taken into account. For those cases in which the activities are not known, and also cases in which it is desired to know the free energy of solution of some solid phase other than the one in equilibrium with the solution at 25°, the free energy may be calculated from the heat of solution (at infinite dilution) and the entropy of solution (hypothetical 1 *M*). The latter quantity is obtained from our values for the entropy of the solid and the aqueous ions. Heats of solution are from Bichowsky and Rossini, corrected to 25° C.

Lithium hydroxide. The ΔH° of solution is -4850 cal.; ΔS° is -10.6 cal. per degree. The ΔF° of solution then is -1690 cal.

Lithium carbonate. The solubility is 0.169 *M*; the activity coefficient is 0.59. One then computes $\Delta F^\circ = 3280$ cal.

Lithium sulfate (anhydrous). ΔH° is -6700 cal.; ΔS°, -21.8 cal.; and ΔF° is -190 cal.

Lithium fluoride. The solubility is 0.10 *M*. The activity coefficient has not been determined up to the saturated solution, but 0.72 would appear to be a fairly good estimate. $\Delta F^\circ = 3120$ cal.

TABLE 32

SUMMARY OF THERMAL DATA USED TO CALCULATE ALKALI METAL POTENTIALS

(Comparison with e.m.f. values)

Metal	S° Element	S° Ion	ΔS°	ΔH°	ΔF°	E° Calc.	E° Exp.
Li	6.7	4.7	13.6	−66,628	−70,700	3.06	2.957
Na	12.2	14.0	17.4	−57,479	−62,685	2.72	2.712
K	15.2	24.2	24.6	−60,270	−67,630	2.93	2.922
Rb	18.1	28.7	26.2	−61,040	−68,890	2.99	2.924
Cs	19.8	31.8	27.6	−62,040	−70,280	3.04	. . .

Lithium chloride. The salt is very soluble; hence the calculation will be made from thermal data. $\Delta H^\circ = -8970$ cal. The estimated entropy of the solid chloride is 16.3. $\Delta S^\circ = 1.9$; $\Delta F^\circ = -9540$ cal.

Sodium hydroxide (anhydrous). $\Delta H^\circ = -10{,}380$ cal.; $\Delta S^\circ = -2.3$ cal. per degree, $\Delta F^\circ = -9700$ cal. From the free energies of the ions, one computes for the free energy of formation of the solid, $-90{,}475$ cal.

Sodium fluoride. Solubility, 1.00 *M*. The activity of the saturated solution has not been determined, but $\gamma = 0.60$ is obtained by extrapolation. $\Delta F^\circ = 610$ cal.

Sodium chloride. Solubility, 6.14 *M*. For the saturated solution γ is 1.013. $\Delta F^\circ = -2165$ cal. The free energy of formation of the solid is $-91{,}770$ cal.

Sodium bromide. The dihydrate is quite soluble but there are not sufficient data to calculate the free energy. For the anhydrous salt, the following calculation can be made: ΔH° is 280 cal. and ΔS° is 12.7 cal. per degree, using an estimated entropy of 21.0 for NaBr. ΔF° of solution then is -3510 cal.

Sodium iodide. No data can be given for the dihydrate. For the anhydrous salt, we find: ΔH°, -1860 cal.; ΔS°, 16.8 cal. (using the estimated entropy of the solid as 22.5); and ΔF°, -6870 cal.

Sodium nitrate. The solubility is 10.83 M and the activity coefficient, 0.355. ΔF° is -1596 cal.

Sodium carbonate. There are not sufficient data to calculate the free energy of solution of the decahydrate. For the anhydrous salt, we find: ΔH°, -6000 cal.; ΔS°, -17.5 cal. per degree; and ΔF°, -780 cal. From the free energies of the ions, one then calculates for the free energy of formation of the solid salt, $-250{,}800$ cal. Kelley and Anderson[3] reported $-251{,}110$ cal. from the heat and entropy of formation of the solid.

Sodium bicarbonate. ΔH° of solution is 3800 cal. and ΔS°, 11.8 cal. per degree. One then calculates for ΔF°, 280 cal.

Sodium sulfate. For the anhydrous salt, we find the following data: ΔH°, -880 cal.; ΔS°, -5.9 cal. per degree (based on an estimate of 38.0 for the entropy of the solid sulfate); and ΔF°, 880 cal.

Potassium hydroxide. The following thermal data may be given for the solution of the anhydrous solid: ΔH°, $-13{,}200$ cal.; ΔS°, 6.5 cal. per degree (entropy of KOH estimated as 15.2); and ΔF°, $-15{,}140$ cal.

Potassium chloride. The solubility is 4.81 M and the activity coefficient for the saturated solution, 0.576. One then computes for ΔF°, -1207 cal. Combining this value with the free energy of the ions, we find the resulting free energy of formation of the solid to be $-97{,}555$ cal.

Potassium bromide. The solubility is 5.68 M and the activity coefficient for the saturated solution, 0.65. One then calculates -1550 cal. for ΔF° of solution. The free energy of the solid salt is $-90{,}450$ cal.

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[3] Kelley, K. K., and Anderson, C. T., U. S. Bur. Mines Bull., No. 384 (1935).

Potassium iodide. ΔH° of solution is 4930 cal.; ΔS° is 25.4 cal. per degree; and ΔF°, -2650 cal.

Potassium sulfate. For the thermal data pertaining to the solution of the salt, we find: ΔH°, 5720 cal.; ΔS°, 7.7 cal. per degree; and ΔF°, 3420 cal.

Potassium nitrate. ΔH° is 8330 cal.; ΔS° is 27.4 cal. per degree; and ΔF° of solution, 140 cal.

Potassium chlorate. The solubility is 0.715 *M* and the activity coefficient for the saturated solution is taken as 0.476. The free energy of solution then is 1277 cal.

Potassium carbonate. ΔH° is -7180 cal.; ΔS°, -0.1 cal. per degree; and ΔF° of solution, -7150 cal.

Potassium perchlorate. The solubility is 0.148 *M* and the activity coefficient for the saturated solution is 0.70. The free energy of solution then is 2690 cal.

Potassium bromate. The solubility is 0.48 *M* and the activity coefficient for the saturated solution is 0.50. The free energy of solution then is 1690 cal.

Potassium iodate. The solubility is 0.43 *M* and the activity coefficient for the saturated solution is 0.52. The free energy of solution then is 1770 cal.

Potassium permanganate. The solubility is 0.482 *M* and the activity coefficient for the saturated solution is 0.49. The free energy of solution then is 1710 cal.

Potassium chloroplatinate. The solubility is 0.0178 *M*, assuming an activity coefficient of 0.7; the ΔF° of solution is 6780 cal.

$$K_2PtCl_6 = 2K^+ + PtCl_6^{--}, \qquad K = 1.1 \times 10^{-5}$$

There are no data on the entropies of rubidium compounds. In the following calculations these values have been estimated by adding 2.3 entropy units per gram atom of rubidium to the entropy of the corresponding potassium compound (cf. Appendix V).

Rubidium hydroxide. The ΔH° of solution is $-14{,}700$ cal. and ΔS° is 8.7 cal. per degree. One then computes for ΔF°, $-17{,}300$ cal.

Rubidium chloride. ΔH° is 4030 cal. and ΔS° is 20.1 cal. per degree. ΔF° then is -1970 cal.

Rubidium sulfate. ΔH° is 6000 cal. and ΔS° is 12.1 cal. per degree. ΔF° is 2370 cal.

Rubidium carbonate. $\Delta H°$ is -9520 cal. and $\Delta S°$, 4.3 cal. per degree. $\Delta F°$ is $-10{,}800$ cal.

Rubidium nitrate. $\Delta H°$ is 9310 cal. and $\Delta S°$, 29.6 cal. per degree. $\Delta F°$ is 470 cal.

Rubidium chlorite. The solubility is 0.392 M; the activity coefficient is 0.52. One then calculates for the free energy of solution, $\Delta F°$, 1880 cal.

Rubidium perchlorate. The solubility is 0.065 M; the activity coefficient, 0.77. $\Delta F°$ is 3560 cal.

There are no data on the entropies of cesium compounds. In the following calculations these values have been estimated by adding 3.6 entropy units per gram atom of cesium to the entropy of the corresponding potassium compound (cf. Appendix V).

TABLE 33

SUMMARY OF FREE ENERGIES OF SOLUTION OF CERTAIN ALKALI COMPOUNDS

(Values in calories)

	OH^-	Cl^-	SO_4^{--}	CO_3^{--}
Li^+	$-1{,}690$	-9540	-190	3,280
Na^+	$-9{,}800$	-2165	880	-780
K^+	$-15{,}140$	-1207	3420	$-7{,}150$
Rb^+	$-17{,}300$	-1970	2370	$-10{,}800$
Cs^+	$-19{,}900$	-2250	-320	$-14{,}780$

Cesium hydroxide. $\Delta H°$ is $-16{,}800$ cal. and $\Delta S°$ is 10.4 cal. per degree. For the free energy of solution, one calculates $\Delta F°$, $-19{,}900$ cal.

Cesium chloride. $\Delta H°$ is 4300 cal. and $\Delta S°$, 21.9 cal. per degree. $\Delta F°$ is -2250 cal.

Cesium sulfate. $\Delta H°$ is 4370 cal. and $\Delta S°$, 15.7 cal. per degree. $\Delta F°$ is -320 cal.

Cesium carbonate. $\Delta H°$ is $-12{,}420$ cal. and $\Delta S°$, 7.9 cal. per degree. $\Delta F°$ is $-14{,}780$ cal.

Cesium nitrate. $\Delta H°$ is 9570 cal. and $\Delta S°$, 31.4 cal. per degree. $\Delta F°$ is 200 cal.

Cesium perchlorate. The solubility is 0.088 M and the activity coefficient of the saturated solution 0.723. $\Delta F°$ of solution is 3270 cal.

Trends in the solubilities of the alkali compounds. In order to note certain trends in the solubilities of the alkali compounds, the data for a few of the more common compounds have been summarized in Table 33. As is to be expected, the free energies of solution of the hydroxides increase regularly with the increasing size of the positive ions. The same is true of the carbonates. The solubilities of both the chloride and sulfate are a minimum for potassium.

APPENDIXES

APPENDIX I

Summary of Oxidation-Reduction Potentials

It is often desirable to know the various couples which have potentials around a given voltage. For this reason a summary, with the couples arranged in order of decreasing E° values, is given. The couples have been separated into two tables, one for acid solutions and one for basic solutions. This has been done, in part, for facility in comparisons and, in part, because the free energy of the completed reactions with the hydrogen couple requires the use of the acid value for this couple in the first case and the alkaline value in the second (see Chapter I). This chapter should also be consulted for the definition of E° and conventions regarding sign. There are, of course, a large number of couples whose potentials are independent of the acid concentration. These might have been listed in a third table, but they have been given in the table for the acid solutions, although a few of the more common are repeated in the table for basic solutions. Values for many additional couples of lesser importance are to be found in the text.

ACID SOLUTIONS

Couple	$E°$
$Li = Li^+ + e^-$	3.02
$Cs = Cs^+ + e^-$	3.02
$Rb = Rb^+ + e^-$	2.99
$K = K^+ + e^-$	2.922
$Ba = Ba^{++} + 2e^-$	2.90
$Sr = Sr^{++} + 2e^-$	2.89
$Ca = Ca^{++} + 2e^-$	2.87
$Na = Na^+ + e^-$	2.712
$La = La^{+++} + 3e^-$	2.37
$Mg = Mg^{++} + 2e^-$	2.34
$H^- = \frac{1}{2}H_2 + e^-$	2.23
$2H_2O + Th = ThO_2 + 4H^+ + 4e^-$	1.80
$Ti = Ti^{++} + 2e^-$	1.75
$Be = Be^{++} + 2e^-$	1.70
$H_2O + Hf = HfO^{++} + 2H^+ + 4e^-$	1.68
$Al = Al^{+++} + 3e^-$	1.67
$2H_2O + Zr = ZrO_2 + 4H^+ + 4e^-$	1.43
$Mn = Mn^{++} + 2e^-$	1.05
$2H_2O + Ti = TiO_2(amorp) + 4H^+ + 4e^-$	0.95
$2H_2O + Si = SiO_2 + 4H^+ + 4e^-$	0.84
$2H_2O + U = UO_2^{++} + 4H^+ + 6e^-$	0.82
$I^- + Tl = TlI + e^-$	0.765
$Zn = Zn^{++} + 2e^-$	0.7620
$2Cl^- + Cr = CrCl_2^- + 3e^-$	0.74
$3H_2O + B = H_3BO_3 + 3H^+ + 3e^-$	0.73
$5H_2O + 2Ta = Ta_2O_5 + 10H^+ + 10e^-$	0.71
$Cr = Cr^{+++} + 3e^-$	0.71
$H_2Te(aq) = Te + 2H^+ + 2e^-$	0.69
$Br^- + Tl = TlBr + e^-$	0.658
$5H_2O + 2Cb = Cb_2O_5 + 10H^+ + 10e^-$	0.62
$H_2O + H_3PO_2 = H_3PO_3 + 2H^+ + 2e^-$	0.59
$Cl^- + Tl = TlCl + e^-$	0.557
$AsH_3 = As + 3H^+ + 3e^-$	0.54
$Ga = Ga^{+++} + 3e^-$	0.52
$H_2C_2O_4(aq) = 2CO_2(g) + 2H^+ + 2e^-$	0.49
$3H_2O + P = H_3PO_3 + 3H^+ + 3e^-$	0.49
$Fe = Fe^{++} + 2e^-$	0.440
$Eu^{++} = Eu^{+++} + e^-$	0.43
$H_2 = 2H^+(10^{-7}\,M) + 2e^-$	0.414
$Cr^{++} = Cr^{+++} + e^-$	0.41
$Cd = Cd^{++} + 2e^-$	0.4020
$2I^- + Pb = PbI_2 + 2e^-$	0.365
$H_2Se(aq) = Se + 2H^+ + 2e^-$	0.36
$SO_4^{--} + Pb = PbSO_4 + 2e^-$	0.355
$In = In^{+++} + 3e^-$	0.340
$Tl = Tl^+ + e^-$	0.3363
$2H_2O + P = H_3PO_2 + H^+ + e^-$	0.29

ACID SOLUTIONS (*Continued*)

Couple	$E°$
$2Br^- + Pb = PbBr_2 + 2e^-$	0.280
$Co = Co^{++} + 2e^-$	0.277
$H_2O + \frac{1}{2}C_2N_2(g) = HCNO + H^+ + e^-$	0.27
$2Cl^- + Pb = PbCl_2 + 2e^-$	0.268
$Ni = Ni^{++} + 2e^-$	0.250
$2H_2O + HS_2O_4^- = 2H_2SO_3 + H^+ + 2e^-$	0.23
$V^{++} = V^{+++} + e^-$	0.20
$H_2O + H_3PO_3 = H_3PO_4 + 2H^+ + 2e^-$	0.20
$I^- + Cu = CuI + e^-$	0.187
$I^- + Ag = AgI + e^-$	0.151
$HCOOH(aq) = CO_2(g) + 2H^+ + 2e^-$	0.14
$Sn = Sn^{++} + 2e^-$	0.136
$H_2O + CH_3CHO(aq) = CH_3COOH(aq) + 2H^+ + 2e^-$	0.13
$Pb = Pb^{++} + 2e^-$	0.126
$2NH_3OH^+ = N_2O + H_2O + 6H^+ + 4e^-$	0.05
$2I^- + 2Hg = Hg_2I_2 + 2e^-$	0.0405
$4I^- + Hg = HgI_4^- + 2e^-$	0.04
$PH_3(g) = P + 3H^+ + 3e^-$	0.04
$Fe = Fe^{+++} + 3e^-$	0.036
$H_2O + HCHO(aq) = HCOOH(aq) + 2H^+ + 2e^-$	0.01
$D_2 = 2D^+ + 2e^-$	0.0034
$2I^- + Cu = CuI_2^- + e^-$	0.00
$H_2 = 2H^+ + 2e^-$	0.000
$2S_2O_3^{--} + Ag = Ag(S_2O_3)_2^{---} + e^-$	−0.01
$H_2O + HCHO(aq) = HCOOH(aq) \mp 2H^+ + 2e^-$	−0.01
$Br^- + Cu = CuBr + e^-$	−0.033
$2Br^- + Cu = CuBr_2^- + e^-$	−0.05
$Br^- + Ag = AgBr + e^-$	−0.073
$H_2O + Ti^{+++} = TiO^{++} + 2H^+ + e^-$	ca −0.1
$Cl^- + Cu = CuCl + e^-$	−0.124
$2Br^- + 2Hg = Hg_2Br_2 + 2e^-$	−0.1397
$H_2S = S + 2H^+ + 2e^-$	−0.141
$4H_2O + Re = ReO_4^- + 8H^+ + 7e^-$	−0.15
$Sn^{++} = Sn^{+4} + 2e^-$	−0.15
$4Cl^- + Bi = BiCl_4^- + 3e^-$	−0.16
$Cu^+ = Cu^{++} + e^-$	−0.167
$2S_2O_3^{--} = S_4O_6^{--} + 2e^-$	−0.17
$2Cl^- + Cu = CuCl_2^- + e^-$	−0.19
$H_2O + H_2SO_3 = SO_4^{--} + 4H^+ + 2e^-$	−0.20
$2H_2SO_3 = S_2O_6^{--} + 4H^+ + 2e^-$	−0.20
$2H_2O + S_2O_6^{--} = 2SO_4^{--} + 4H^+ + 2e^-$	−0.20
$4Br^- + Hg = HgBr_4^{--} + 2e^-$	−0.21
$Sb + H_2O = SbO^+ + 2H^+ + 3e^-$	−0.212
$Cl^- + Ag = AgCl + e^-$	−0.2222
$CH_3OH(aq) = HCHO(aq) + 2H^+ + 2e^-$	−0.24
$2H_2O + As = HAsO_2(aq) + 3H^+ + 3e^-$	−0.2475
$2Cl^- + 2Hg = Hg_2Cl_2 + 2e^-$	−0.2676
$2SO_3^{--} + Ag = Ag(SO_3)_2^{---} + e^-$	−0.30

ACID SOLUTIONS (*Continued*)

Couple	E°
$H_2O + V^{+++} = VO^{++} + H^+ + e^-$	−0.314
$H_2O + Bi = BiO^+ + 2H^+ + 3e^-$	−0.32
$UO_2 = UO_2^{++} + 2e^-$	−0.33
$HCN = \frac{1}{2}C_2N_2(g) + H^+ + e^-$	−0.33
$Cu = Cu^{++} + 2e^-$	−0.3448
$Fe(CN)_6^{-4} = Fe(CN)_6^{---} + e^-$	−0.36
$IO_3^- + Ag = AgIO_3 + e^-$	−0.37
$4Cl^- + Hg = HgCl_4^{--} + 2e^-$	−0.38
$2IO_3^- + Hg = Hg(IO_3)_2(s) + 2e^-$	−0.40
$3H_2O + S_2O_3^{--} = 2H_2SO_3 + 2H^+ + 4e^-$	−0.40
$2NH_3OH^+ = H_2N_2O_2 + 6H^+ + 4e^-$	−0.44
$3H_2O + S = H_2SO_3 + 4H^+ + 4e^-$	−0.45
$6H_2O + S_4O_6^{--} = 4H_2SO_3 + 4H^+ + 6e^-$	−0.48
$I^- + Au = AuI + e^-$	−0.50
$Cu = Cu^+ + e^-$	−0.522
$2H_2O + Te = TeO_2(s) + 4H^+ + 4e^-$	−0.529
$2I^- = I_2 + 2e^-$	−0.5345
$3I^- = I_3^- + 2e^-$	−0.5355
$BrO_3^- + Ag = AgBrO_3 + e^-$	−0.55
$2H_2O + HAsO_2 = H_3AsO_4 + 2H^+ + 2e^-$	−0.559
$2H_2O + Te = TeO_2H^+ + 3H^+ + 4e^-$	−0.559
$CuCl = Cu^{++} + Cl^- + e^-$	−0.566
$H_2O + CH_4(g) = CH_3OH(aq) + 2H^+ + 2e^-$	−0.58
$H_2N_2O_2 = 2NO + 2H^+ + 2e^-$	−0.60
$SO_4^{--} + 2Hg = Hg_2SO_4 + 2e^-$	−0.6151
$2Br^- + PtBr_4^{--} = PtBr_6^{--} + 2e^-$	−0.63
$4Cl^- + Pd = PdCl_4^{--} + 2e^-$	−0.64
$3H_2O + 2SbO^+ = Sb_2O_5 + 6H^+ + 4e^-$	−0.64
$SO_4^{--} + 2Ag = Ag_2SO_4 + 2e^-$	−0.653
$CuBr = Cu^{++} + Br^- + e^-$	−0.657
$3NH_4^+ = HN_3 + 11H^+ + 8e^-$	−0.66
$2H_2O + 2SbO^+ = Sb_2O_4 + 4H^+ + 2e^-$	−0.68
$3H_2O + S_3O_6^{--} = 3H_2SO_3 + 2e^-$	−0.68
$H_2O_2 = O_2 + 2H^+ + 2e^-$	−0.682
$CuI_2^- = Cu^{++} + 2I^- + e^-$	−0.690
$2Cl^- + PtCl_4^{--} = PtCl_6^{--} + 2e^-$	−0.72
$6Cl^- + Ir = IrCl_6^{---} + 3e^-$	−0.72
$4Cl^- + Pt = PtCl_4^{--} + 2e^-$	−0.73
$Se + 3H_2O = H_2SeO_3 + 4H^+ + 4e^-$	−0.740
$2CNS^- = (CNS)_2 + 2e^-$	−0.77
$Fe^{++} = Fe^{+++} + e^-$	−0.771
$2Hg = Hg_2^{++} + 2e^-$	−0.7986
$Ag = Ag^+ + e^-$	−0.7995
$H_2N_2O_2 + 2H_2O = 2HNO_2 + 4H^+ + 4e^-$	−0.80
$2H_2O + N_2O_4 = 2NO_3^- + 4H^+ + 2e^-$	−0.81
$2H_2O = O_2 + 4H^+(10^{-7}M) + 4e^-$	−0.815
$2Br^- + AuBr_2^- = AuBr_4^- + 2e^-$	−0.82
$Pd = Pd^{++} + 2e^-$	−0.83

ACID SOLUTIONS (*Continued*)

Couple	$E°$
$4H_2O + Os = OsO_4(s) + 8H^+ + 8e^-$	-0.85
$Hg = Hg^{++} + 2e^-$	-0.854
$4Br^- + Au = AuBr_4^- + 3e^-$	-0.87
$CuI = Cu^{++} + I^- + e^-$	-0.877
$Hg_2^{++} = 2Hg^{++} + 2e^-$	-0.910
$HNO_2 + H_2O = NO_3^- + 3H^+ + 2e^-$	-0.94
$2H_2O + NO = NO_3^- + 4H^+ + 3e^-$	-0.96
$2Br^- + Au = AuBr_2^- + e^-$	-0.96
$NO + H_2O = HNO_2 + H^+ + e^-$	-0.99
$H_2O + I^- = HIO + H^+ + 2e^-$	-0.99
$2H_2O + Pt = Pt(OH)_2 + 2H^+ + 2e^-$	-0.99
$3H_2O + VO^{++} = V(OH)_4^+ + 2H^+ + e^-$	-1.000
$4Cl^- + Au = AuCl_4^- + 3e^-$	-1.00
$ClO_3^- + H_2O = 2H^+ + ClO_4^- + 2e^-$	-1.00
$4H_2O + TeO_2(s) = H_6TeO_6(s) + 2H^+ + 2e^-$	-1.02
$IrCl_6^{---} = IrCl_6^{--} + e^-$	-1.021
$H_2O + S_2O_3^{--} = HS_2O_4^- + H^+ + 2e^-$	-1.03
$2H_2O + 2NO = N_2O_4 + 4H^+ + 4e^-$	-1.03
$3Br^- = Br_3^- + 2e^-$	-1.05
$2Cl^- + \frac{1}{2}I_2 = ICl_2^- + e^-$	-1.06
$2Br^- = Br_2(l) + 2e^-$	-1.0652
$2HNO_2 = N_2O_4 + 2H^+ + 2e^-$	-1.07
$3H_2O + I^- = IO_3^- + 6H^+ + 6e^-$	-1.085
$2Br^- = Br_2(aq) + 2e^-$	-1.087
$H_2O + H_2SeO_3 = SeO_4^{--} + 4H^+ + 2e^-$	-1.15
$\frac{1}{2}I_2 + 3H_2O = IO_3^- + 6H^+ + 5e^-$	-1.195
$Pt = Pt^{++} + 2e^-$	ca -1.2
$2H_2O = O_2 + 4H^+ + 4e^-$	-1.229
$HClO_2 + H_2O = 3H^+ + ClO_3^- + 2e^-$	-1.23
$2NH_4^+ = N_2H_5^+ + 3H^+ + 2e^-$	-1.24
$Tl^+ = Tl^{+++} + 2e^-$	-1.25
$2H_2O + Mn^{++} = MnO_2 + 4H^+ + 2e^-$	-1.28
$PdCl_4^{--} + 2Cl^- = PdCl_6^{--} + 2e^-$	-1.288
$N_2O + 3H_2O = 2HNO_2 + 4H^+ + 4e^-$	-1.29
$Au^+ = Au^{+++} + 2e^-$	ca -1.29
$H_2O + Br^- = HBrO + H^+ + 2e^-$	-1.33
$\frac{1}{2}Cl_2 + 4H_2O = 8H^+ + ClO_4^- + 7e^-$	-1.34
$H_2O + NH_4^+ = NH_3OH^+ + 2H^+ + 2e^-$	-1.35
$Cl^- = \frac{1}{2}Cl_2 + e^-$	-1.3583
$TlCl = Tl^{+++} + Cl^- + 2e^-$	-1.36
$7H_2O + 2Cr^{+++} = Cr_2O_7^{--} + 14H^+ + 6e^-$	-1.36
$3H_2O + 2Au = Au_2O_3 + 6H^+ + 6e^-$	-1.363
$H_2O + Rh^{+++} = RhO^{++} + 2H^+ + e^-$	-1.40
$Au = Au^{+++} + 3e^-$	-1.42
$3H_2O + Br^- = BrO_3^- + 6H^+ + 6e^-$	-1.44
$\frac{1}{2}I_2 + H_2O = HIO + H^+ + e^-$	-1.45
$3H_2O + Cl^- = ClO_3^- + 6H^+ + 6e^-$	-1.45
$2H_2O + Pb^{++} = PbO_2 + 4H^+ + 2e^-$	-1.456

ACID SOLUTIONS (*Concluded*)

Couple	$E°$
$3H_2O + RhO^{++} = RhO_4^{--} + 6H^+ + 2e^-$	−1.46
$N_2H_5^+ + 2H_2O = 2NH_3OH^+ + H^+ + 2e^-$	−1.46
$\frac{1}{2}Cl_2 + 3H_2O = 6H^+ + ClO_3^- + 5e^-$	−1.47
$H_2O + Cl^- = HClO + H^+ + 2e^-$	−1.49
$Mn^{++} = Mn^{+++} + e^-$	−1.51
$\frac{1}{2}Br_2 + 3H_2O = BrO_3^- + 6H^+ + 5e^-$	−1.52
$4H_2O + Mn^{++} = MnO_4^- + 8H^+ + 5e^-$	−1.52
$2H_2O + Cl^- = HClO_2 + 3H^+ + 4e^-$	−1.56
$2H_2O + 2BiO^+ = Bi_2O_4 + 4H^+ + 2e^-$	ca −1.59
$\frac{1}{2}Br_2 + H_2O = HBrO + H^+ + e^-$	−1.59
$N_2O + H_2O = 2NO + 2H^+ + 2e^-$	−1.59
$Ce^{+3} = Ce^{+4} + e^-$	−1.61
$\frac{1}{2}Cl_2 + H_2O = H^+ + HClO + e^-$	−1.63
$\frac{1}{2}Cl_2 + 2H_2O = 3H^+ + HClO_2 + 3e^-$	−1.63
$2H_2O + MnO_2 = MnO_4^- + 4H^+ + 3e^-$	−1.67
$Au = Au^+ + e^-$	−1.68
$2H_2O + PbSO_4 = PbO_2 + SO_4^{--} + 4H^+ + 2e^-$	−1.685
$Pb^{++} = Pb^{+4} + 2e^-$	−1.69
$3H_2O + IO_3^- = H_5IO_6 + H^+ + 2e^-$	ca −1.7
$2H_2O + Ni^{++} = NiO_2 + 4H^+ + 2e^-$	−1.75
$2H_2O = H_2O_2 + 2H^+ + 2e^-$	−1.77
$N_2 + H_2O = N_2O + 2H^+ + 2e^-$	−1.77
$NH_4^+ + N_2 = HN_3 + 3H^+ + 2e^-$	−1.82
$Co^{++} = Co^{+++} + e^-$	−1.84
$Ag^+ = Ag^{++} + e^-$	−1.98
$2SO_4^{--} = S_2O_8^{--} + 2e^-$	−2.05
$O_2 + H_2O = O_3 + 2H^+ + 2e^-$	−2.07
$H_2O + 2F^- = F_2O + 2H^+ + 4e^-$	−2.1
$H_2O = OH + H^+ + e^-$	−2.2
$H_2O = O(g) + 2H^+ + 2e^-$	−2.42
$2F^- = F_2 + 2e^-$	−2.85
$2HF = F_2 + 2H^+ + 2e^-$	−3.03

BASIC SOLUTIONS

Couple	$E°$
$Li = Li^+ + e^-$	3.02
$Cs = Cs^+ + e^{-*}$	3.02
$2OH^- + Ca = Ca(OH)_2 + 2e^-$	3.02
$8H_2O + 2OH^- + Sr = Sr(OH)_2 \cdot 8H_2O + 2e^-$	2.99
$Rb = Rb^+ + e^-$	2.99
$8H_2O + 2OH^- + Ba = Ba(OH)_2 \cdot 8H_2O + 2e^-$	2.97
$K = K^+ + e^-$	2.922
$3OH^- + La = La(OH)_3 + 3e^-$	2.76
$Na = Na^+ + e^-$	2.712
$2OH^- + Mg = Mg(OH)_2 + 2e^-$	2.67

BASIC SOLUTIONS (*Continued*)

Couple	$E°$
$4OH^- + Th = ThO_2 + 2H_2O + 4e^-$	2.64
$4OH^- + Hf = HfO(OH)_2 + H_2O + 4e^-$	2.60
$4OH^- + B = H_2BO_3^- + 2H_2O + 3e^-$	2.5
$4OH^- + Al = H_2AlO_3^- + H_2O + 3e^-$	2.35
$4OH^- + Zr = H_2ZrO_3 + H_2O + 4e^-$	2.32
$6OH^- + 2Be = Be_2O_3^{--} + 3H_2O + 4e^-$	2.28
$2OH^- + P = H_2PO_2^- + e^-$	1.82
$5OH^- + P = HPO_3^{--} + 2H_2O + 3e^-$	1.71
$6OH^- + Si = SiO_3^{--} + 3H_2O + 4e^-$	1.73
$3OH^- + H_2PO_2^- = HPO_3^{--} + 2H_2O + 2e^-$	1.65
$2OH^- + Mn = Mn(OH)_2 + 2e^-$	1.47
$S^{--} + Zn = ZnS + 2e^-$	1.44
$4OH^- + S_2O_4^{--} = 2SO_3^{--} + 2H_2O + 2e^-$	1.4
$3OH^- + AsH_3 = As + 3H_2O + 3e^-$	1.37
$CO_3^{--} + Mn = MnCO_3 + 2e^-$	1.35
$3OH^- + Cr = Cr(OH)_3 + 3e^-$	1.3
$4CN^- + Zn = Zn(CN)_4^{--} + 2e^-$	1.26
$S^{--} + Cd = CdS + 2e^-$	1.23
$4OH^- + Ga = H_2GaO_3^- + H_2O + 3e^-$	1.22
$4OH^- + Zn = ZnO_2^{--} + 2H_2O + 2e^-$	1.216
$4OH^- + Cr = CrO_2^- + 2H_2O + 3e^-$	1.2
$HCHO(aq) + 3OH^- = HCO_2^- (aq) + 2H_2O + 2e^-$	1.14
$S^{--} + Ni = NiS(\gamma) + 2e^-$	1.07
$CO_3^{--} + Zn = ZnCO_3 + 2e^-$	1.07
$3OH^- + HPO_3^{--} = PO_4^{---} + 2H_2O + 2e^-$	1.05
$2NH_2OH + 4OH^- = N_2O + 5H_2O + 4e^-$	1.05
$S^{--} + 2Tl = Tl_2S + 2e^-$	1.04
$4NH_3(aq) + Zn = Zn(NH_3)_4^{++} + 2e^-$	1.03
$S^{--} + Fe = FeS + 2e^-$	1.00
$S^{--} + Pb = PbS + 2e^-$	0.98
$2OH^- + CN^- = CNO^- + H_2O + 2e^-$	0.96
$H_2O + 3OH^- + HSnO_2^- = Sn(OH)_6^{--} + 2e^-$	0.96
$S^{--} + 2Cu = Cu_2S + 2e^-$	0.95
$HCO_2^- + 3OH^- = CO_3^{--} + 2H_2O + 2e^-$	0.95
$S^{--} + Co = CoS(\alpha) + 2e^-$	0.93
$Te^{--} = Te + 2e^-$	0.92
$4CN^- + Cd = Cd(CN)_4^{--} + 2e^-$	0.90
$2OH^- + SO_3^{--} = SO_4^{--} + H_2O + 2e^-$	0.90
$3OH^- + PH_3(g) = P + 3H_2O + 3e^-$	0.87
$2OH^- + Fe = Fe(OH)_2 + 2e^-$	0.877
$S^{--} + Ni = NiS(\alpha) + 2e^-$	0.86
$4OH^- + N_2O_4 = 2NO_3^- + 2H_2O + 2e^-$	0.85
$Co(CN)_6^{-4} = Co(CN)_6^{---} + e^-$	0.83
$S^{--} + Pt = PtS + 2e^-$	0.83
$H_2 + 2OH^- = 2H_2O + 2e^-$	0.828
$CN^- + Ni(CN)_3^{--} = Ni(CN)_4^{--} + e^-$	0.82
$2OH^- + Cd = Cd(OH)_2 + 2e^-$	0.815
$8OH^- + Re = ReO_4^- + 4H_2O + 7e^-$	0.81
$CO_3^{--} + Cd = CdCO_3 + 2e^-$	0.80

BASIC SOLUTIONS (*Continued*)

Couple	E°
$3OH^- + Sn = HSnO_2^- + H_2O + 2e^-$	0.79
$Se^{--} = Se + 2e^-$	0.78
$S^{--} + Cu = CuS + 2e^-$	0.76
$CO_3^{--} + Fe = FeCO_3 + 2e^-$	0.755
$2OH^- + Co = Co(OH)_2 + 2e^-$	0.73
$2NH_2OH + 6OH^- = N_2O_2^{--} + 6H_2O + 4e^-$	0.73
$S^{--} + 2Ag = Ag_2S + 2e^-$	0.71
$4OH^- + AsO_2^- = AsO_4^{---} + 2H_2O + 2e^-$	0.71
$S^{--} + Hg = HgS + 2e^-$	0.70
$4OH^- + As = AsO_2^- + 2H_2O + 3e^-$	0.68
$4OH^- + Sb = SbO_2^- + 2H_2O + 3e^-$	0.66
$2OH^- + Ni = Ni(OH)_2 + 2e^-$	0.66
$CO_3^{--} + Co = CoCO_3 + 2e^-$	0.632
$6OH^- + S^{--} = SO_3^{--} + 3H_2O + 6e^-$	0.61
$2CN^- + Au = Au(CN)_2^- + e^-$	0.60
$4NH_3 + Cd = Cd(NH_3)_4^{++} + 2e^-$	0.597
$CH_3OH(aq) + 2OH^- = HCHO(aq) + 2H_2O + 2e^-$	0.59
$6OH^- + S_2O_3^{--} = 2SO_3^{--} + 3H_2O + 4e^-$	0.58
$2OH^- + Pb = PbO(r) + H_2O + 2e^-$	0.578
$OH^- + Fe(OH)_2 = Fe(OH)_3 + e^-$	0.56
$S^{--} + S_3^{--} = S_4^{--} + 2e^-$	0.55
$3OH^- + Pb = HPbO_2^- + H_2O + 2e^-$	0.54
$S^{--} + S_2^{--} = S_3^{--} + 2e^-$	0.52
$2S^{--} = S_2^{--} + 2e^-$	0.51
$S^{--} = S + 2e^-$	0.508
$CO_3^{--} + Pb = PbCO_3 + 2e^-$	0.506
$6NH_3(aq) + Ni = Ni(NH_3)_6^{++} + 2e^-$	0.48
$OH^- + HS^- = S + H_2O + 2e^-$	0.478
$NO + 2OH^- = NO_2^- + H_2O + e^-$	0.46
$3OH^- + Bi = BiOOH + H_2O + 3e^-$	0.46
$CO_3^{--} + Ni = NiCO_3 + 2e^-$	0.45
$6NH_3(aq) + Co = Co(NH_3)_6^{++} + 2e^-$	0.422
$OH^- + Mn(OH)_2 = Mn(OH)_3 + e^-$	0.40
$4CN^- + Hg = Hg(CN)_4^{--} + 2e^-$	0.37
$2OH^- + 2Cu = Cu_2O + H_2O + 2e^-$	0.361
$6OH^- + Se = SeO_3^{--} + 3H_2O + 4e^-$	0.35
$OH^- + Tl = Tl(OH) + e^-$	0.3445
$2CN^- + Ag = Ag(CN)_2^- + e^-$	0.29
$CH_4(g) + 2OH^- = CH_3OH(aq) + H_2O + 2e^-$	0.25
$2OH^- + Cu = Cu(OH)_2 + 2e^-$	0.224
$N_2O_2^{--} + 4OH^- = 2NO_2^- + 2H_2O + 4e^-$	0.18
$5OH^- + Cr(OH)_3 = CrO_4^{--} + 4H_2O + 3e^-$	0.12
$2NH_3 + Cu = Cu(NH_3)_2^+ + e^-$	0.11
$H_2O + 2OH^- + Cu_2O = 2Cu(OH)_2 + 2e^-$	0.09
$OH^- + HO_2^- = O_2 + H_2O + 2e^-$	0.076
$4NH_3 + Cu = Cu(NH_3)_4^{++} + 2e^-$	0.05
$2OH^- + Tl(OH) = Tl(OH)_3 + 2e^-$	0.05
$CN^- + Ag = AgCN + e^-$	0.04
$6OH^- + Te = TeO_3^{--} + 2H_2O + 4e^-$	0.02

BASIC SOLUTIONS (*Concluded*)

Couple	E°
$2NH_3 + Cu(NH_3)_2^+ = Cu(NH_3)_4^{++} + e^-$	0.0
$2OH^- + NO_2^- = NO_3^- + H_2O + 2e^-$	−0.01
$2OH^- + SeO_3^{--} = SeO_4^{--} + H_2O + 2e^-$	−0.03
$CO_3^{--} + Cu = CuCO_3 + 2e^-$	−0.053
$CNS^- + Ag = AgCNS + e^-$	−0.09
$Hg + 2OH^- = HgO(r) + H_2O + 2e^-$	−0.0984
$2OH^- + Pd = Pd(OH)_2 + 2e^-$	−0.1
$2OH^- + 2NH_4OH = N_2H_4 + 4H_2O + 2e^-$	−0.1
$6OH^- + 2Ir = Ir_2O_3 + 3H_2O + 6e^-$	−0.1
$Co(NH_3)_6^{++} = Co(NH_3)_6^{+++} + e^-$	−0.1
$N_2O_2^{--} = 2NO + 2e^-$	−0.10
$2OH^- + 2Hg = Hg_2O + H_2O + 2e^-$	−0.123
$N_2O + 6OH^- = 2NO_2^- + 3H_2O + 4e^-$	−0.15
$2OH^- + Pt = Pt(OH)_2 + 2e^-$	−0.16
$2OH^- + ClO_3^- = ClO_4^- + H_2O + 2e^-$	−0.17
$OH^- + Co(OH)_2 = Co(OH)_3 + e^-$	−0.2
$6OH^- + I^- = IO_3^- + 3H_2O + 6e^-$	−0.26
$CO_3^{--} + 2Hg = Hg_2CO_3 + 2e^-$	−0.32
$2OH^- + 2Ag = Ag_2O + H_2O + 2e^-$	−0.344
$2OH^- + ClO_2^- = ClO_3^- + H_2O + 2e^-$	−0.35
$2NH_3(aq) + Ag = Ag(NH_3)_2^+ + e^-$	−0.373
$4OH^- = O_2 + 2H_2O + 4e^-$	−0.401
$NH_4OH + 2OH^- = NH_2OH + 2H_2O + 2e^-$	−0.42
$CrO_4^{--} + 2Ag = Ag_2CrO_4 + 2e^-$	−0.446
$CO_3^{--} + 2Ag = Ag_2CO_3 + 2e^-$	−0.47
$2OH^- + Ni(OH)_2 = NiO_2 + 2H_2O + 2e^-$	−0.49
$2OH^- + I^- = IO^- + H_2O + 2e^-$	−0.49
$MnO_4^{--} = MnO_4^- + e^-$	−0.54
$4OH^- + IO^- = IO_3^- + 2H_2O + 4e^-$	−0.56
$4OH^- + MnO_2 = MnO_4^- + 2H_2O + 3e^-$	−0.57
$2OH^- + Ag_2O = 2AgO + H_2O + 2e^-$	−0.57
$4OH^- + MnO_2 = MnO_4^{--} + 2H_2O + 2e^-$	−0.58
$2OH^- + ClO^- = ClO_2^- + H_2O + 2e^-$	−0.59
$6OH^- + Br^- = BrO_3^- + 3H_2O + 6e^-$	−0.61
$6OH^- + Cl^- = ClO_3^- + 3H_2O + 6e^-$	−0.62
$2CNS^- + Au(CNS)_2^- = Au(CNS)_4^- + 2e^-$	−0.645
$2CNS^- + Au = Au(CNS)_2^- + e^-$	−0.69
$3OH^- + IO_3^- = H_3IO_6^{--} + 2e^-$	ca −0.70
$N_2H_4 + 2OH^- = 2NH_2OH + 2e^-$	−0.74
$2OH^- + 2AgO = Ag_2O_3 + H_2O + 2e^-$	−0.74
$4OH^- + Cl^- = ClO_2^- + 2H_2O + 4e^-$	−0.76
$N_2O + 2OH^- = 2NO + H_2O + 2e^-$	−0.76
$2OH^- + Br^- = BrO^- + H_2O + 2e^-$	−0.76
$3OH^- = HO_2^- + H_2O + 2e^-$	−0.87
$2NO_2^- = N_2O_4 + 2e^-$	−0.88
$2OH^- + Cl^- = ClO^- + H_2O + 2e^-$	−0.94
$ClO_2^- = ClO_2 + e^-$	−1.15
$O_2 + 2OH^- = O_3 + H_2O + 2e^-$	−1.24
$OH^- = OH + e^-$	−1.4

APPENDIX II

Summary of Free Energies of Formation

Note: Values, in calories, are for 25° C. See Chapter I for definitions. This table summarizes the more important free energies but many additional values may be calculated from the data in the text.

Substance	ΔF°	Substance	ΔF°
Aluminum		**Barium** (*Cont.*)	
Al(g)	57,785	BaH_2	−31,500
Al^{+++}	−115,500	$Ba(OH)_2 \cdot 8H_2O$	−665,680
$Al(OH)_3$	−272,900	$BaCO_3$	−271,570
$H_2AlO_3^-$	−256,000	BaO_2	−138,000
AlF_6^{---}	−542,000	**Beryllium**	
Antimony		Be^{++}	−78,700
Sb(g)	44,000	$Be_2O(OH)_2$	−305,610
Sb_2(g)	40,000	$Be_2O_3^{--}$	−265,810
SbH_3(g)	35,300	**Bismuth**	
Sb_2O_3(s)	−149,030	BiO^+	−34,550
SbO^+	−42,000	Bi_2O_3(s)	−116,600
$HSbO_2$(aq)	−97,500	BiOOH(s)	−87,800
SbO_2^-	−82,500	BiOCl(s)	−77,000
Sb_2O_5(s)	−195,500	$BiCl_3$(s)	−76,400
Sb_2O_4(s)	−165,900	$BiCl_4^-$	−114,200
$SbCl_3$(s)	−77,800	BiO(s)	−43,200
Sb_2S_3(s)	−35,700	Bi(g)	38,500
Arsenic		Bi_2O_4	ca −109,000
As(g)	20,400	**Boron**	
As_4(g)	20,500	H_3BO_3	−220,600
AsH_3(g)	37,700	$H_2BO_3^-$	ca −208,000
As_2O_3(s)	−137,670	BF_4^-	−335,900
$HAsO_2$(aq)	−96,345	**Bromine**	
H_3AsO_3(aq)	−153,035	Br(g)	19,900
AsO_2^-	−83,770	Br_2(aq)	977
AsO^+	−39,260	Br_2(g)	755
H_3AsO_4(aq)	−183,930	Br_2(s)	314
$H_2AsO_4^-$	−180,700	Br^-	−24,578
$HAsO_4^{--}$	−171,100	Br_3^-	−25,270
AsO_4^{---}	−153,400	HBrO	−19,900
As_2S_3	−20,000	BrO^-	−8,000
AsS_2^-	−6,000	BrO_3^-	5,000
$AsCl_3$(l)	−65,190	BrCl(g)	−530
Barium		**Cadmium**	
Ba^{++}	−133,850	Cd(g)	18,489

Substance	ΔF°	Substance	ΔF°
Cadmium (*Cont.*)		**Carbon** (*Cont.*)	
Cd^{++}	−18,550	$HCN(aq)$	26,340
$Cd(OH)_2(s)$	−112,730	CN^-	39,140
$Cd(NH_3)_4^{++}$	−52,850	$C_2N_2(g)$	67,780
$Cd(CN)_4^{--}$	111,000	$HCNO$	−28,980
CdS	−33,100	CNO^-	−23,630
$CdCO_3$	−163,410	$HCNS$	17,800
Calcium		CNS^-	23,140
$Ca(g)$	34,508	$COCl_2(g)$	−48,960
Ca^{++}	−132,700	CCl_4	−15,600
CaH_2	−35,700	$COS(g)$	−39,800
$Ca(OH)_2$	−214,830	$CS_2(l)$	17,150
$CaCO_3$	−207,430	$CO(NH_2)_2(aq)$	−48,720
CaO_2	−142,000	**Cesium**	
Carbon		$Cs(g)$	12,231
$C(g)$	187,430	Cs^+	−70,280
$C_2(g)$	222,830	CsH	−7,300
$CO(g)$	−33,010	**Chlorine**	
$CO_2(g)$	−94,450	$Cl(g)$	25,900
H_2CO_3	−149,170	$Cl_2(aq)$	1,630
HCO_3^-	−140,490	Cl^-	−31,330
CO_3^{--}	−126,390	ClO^-	−9,200
$CH_4(g)$	−12,200	$HClO$	−19,110
$C_2H_6(g)$	−10,700	$HClO_2$	−600
$C_2H_4(g)$	12,300	ClO_2^-	2100
C_2H_2	50,750	$ClO_2(g)$	28,600
$C_6H_5CH_3(l)$	26,800	ClO_3^-	−250
$CH_3OH(l)$	−39,960	ClO_4^-	−10,700
$CH_3OH(aq)$	−42,110	**Chromium**	
$HCHO(aq)$	−31,020	$Cr(g)$	78,630
$HCOOH(l)$	−85,150	Cr^{+++}	−49,000
$HCOOH(aq)$	−88,110	$CrCl_2^+$	−114,100
$HCOO^-$	−83,000	$Cr(OH)_3$	ca −202,750
$C_2H_5OH(l)$	−40,200	CrO_2^-	−123,000
$C_2H_5OH(aq)$	−41,850	Cr^{++}	−39,400
$CH_3CHO(l)$	−31,880	CrO_4^{--}	−171,400
$CH_3CHO(aq)$	(−33,560)	$HCrO_4^-$	−180,250
$CH_3COOH(l)$	−94,500	$Cr_2O_7^{--}$	−306,000
$CH_3COOH(aq)$	−96,210	CrO_2Cl_2	−117,000
CH_3COO^-	−89,720	**Cobalt**	
$H_2C_2O_4(aq)$	−166,060	Co^{++}	−12,800
$HC_2O_4^-$	−164,380	$Co(OH)_2$	−108,900
$C_2O_4^{--}$	−158,660	$Co(NH)_6^{++}$	−57,470
$C_6H_5COOH(s)$	−60,100	$CoS(\alpha)$	−19,800
C_6H_5COOH (aq)	−57,950	$CoCO_3$	−155,570
$C_6H_5COO^-$	−52,250	Co^{+++}	28,900
$C_6H_{12}O_6(aq)$	−217,020	$Co(OH)_3$	−142,000
$C_6H_5NH_2(l)$	35,400	$Co(NH_3)_6^{+++}$	−55,000
$C_6H_5NH_3^+$	29,400	$Co(NH_3)_5 \cdot H_2O^{+++}$	−106,000
$HCN(g)$	27,730		

Substance	ΔF°	Substance	ΔF°
Columbium		**Indium**	
Cb_2O_5	−425,800	In(g)	44,000
Copper		In^{+++}	−23,500
Cu(g)	71,700	In_2O_3	−21,800
Cu^+	12,040	InCl	−39,200
Cu_2O	−35,150	**Iodine**	
CuCl	−28,490	I(g)	16,870
CuBr	−23,812	$I_2(g)$	4,630
CuI	−16,658	$I_2(aq)$	3,926
$CuCl_2^-$	−58,300	I^-	−12,333
$CuBr_2^-$	−45,000	I_3^-	−12,290
CuI_2^-	−24,600	HIO	−23,330
$Cu_2S(\alpha)$	−20,200	IO^-	−8,300
Cu^{++}	15,910	ICl(s)	−4,000
CuO	−30,400	ICl_2^-	−38,350
$Cu(OH)_2$	−85,500	$ICl_3(s)$	−21,150
$HCuO_2^-$	−61,325	IO_3^-	−32,251
CuO_2^{--}	−43,310	H_5IO_6	ca −123,900
CuS	−11,755	IBr(aq)	−900
$CuCO_3$	−123,930	IBr_2^-	−28,970
Fluorine		**Iridium**	
F(g)	27,600	Ir(g)	105,000
F^-	−65,700	IrCl	−16,900
HF(aq)	−70,000	$IrCl_2$	−32,000
$F_2O(g)$	9,500	$IrCl_3$	−46,500
Gallium		$IrCl_6^{---}$	−137,800
Ga(g)	43,200	IrO_2	−28,000
Ga^{+++}	−36,000	**Iron**	
$Ga(OH)_3$	ca −198,300	Fe(g)	85,682
$H_2GaO_3^-$	ca −178,000	Fe^{++}	−20,310
Ga_2O_3	−235,000	$Fe(OH)_2$	−115,660
Ga^{++}	ca −21,000	$FeCO_3$	−161,260
Ga_2O	−75,200	FeS	−22,900
Germanium		Fe^{+++}	−2,530
GeO_2	−142,000	$Fe(OH)_3$	−166,300
Gold		Fe_2S_3	−55,000
Au(g)	82,500	**Lanthanum**	
Au_2O_3	18,710	La^{+++}	ca −163,800
Au^{+++}	98,200	$La(OH)_3$	ca −303,800
AuI	−760	**Lead**	
Au^+	ca 38,700	Pb(g)	39,600
$AuCl_4^-$	−56,200	Pb^{++}	−5,810
Hafnium		PbO(red)	−45,100
HfO_2	−258,200	PbO(yellow)	−44,956
HfO^{++}	−212,100	$PbO\cdot 1/3H_2O$	−63,721
Hydrogen		$HPbO_2^-$	−80,800
H(g)	48,350	$Pb(OH)_2$	−102,200
H^+	0	$PbCl_2$	−75,040
H^-	51,500	$PbBr_2$	−62,060
		PbI_2	−41,470

Substance	ΔF°	Substance	ΔF°
Lead (*Cont.*)		**Molybdenum** (*Cont.*)	
PbS	−21,910	MoO_4^{--}	−208,000
$PbSO_4$	−159,500	MoO_3	−157,600
$PbCO_3$	−149,710	MoO_2	−118,000
$PbO \cdot PbCO_3$	−195,240	Mo^{+++}	ca −13,800
$Pb_3(CO_3)_2(OH)_2$	−409,115	H_2MoO_4	ca −227,000
PbO_2	−52,020	**Nickel**	
Pb^{+4}	ca 72,200	Ni(g)	87,433
Pb_3O_4	−142,210	Ni^{++}	−11,530
Lithium		$Ni(OH)_2$	−105,600
Li(g)	28,807	**Nitrogen**	
Li^+	−70,700	N(g)	81,000
LiH	−16,900	NO(g)	20,660
Li_2O_2	−138,000	N_2O(g)	24,930
Magnesium		NO_2(g)	12,274
Mg(g)	27,640	N_2O_4(g)	23,440
Mg^{++}	−107,780	NO_3^-	−26,250
$Mg(OH)_2$	−193,300	HNO_2	−13,020
MgO	−136,370	NO_2^-	−8,450
$MgCO_3$	−246,630	NH_2OH(aq)	−5,600
Manganese		NH_3OH^+	−13,540
Mn(g)	59,535	NH_3(g)	−3,940
Mn^{++}	−48,600	NH_3(aq)	−6,330
$Mn(OH)_2$	−143,100	NH_4OH(aq)	−62,990
MnS	−46,000	NH_4^+	−18,960
$Mn(OH)_3$	ca −190,000	$H_2N_2O_2$(aq)	ca 13,600
MnO_4^-	−100,600	$N_2O_2^{--}$	ca 36,650
MnO_2	−102,900	N_2H_4	29,800
MnO_4^{--}	−113,100	$N_2H_5^+$	18,950
Mercury		$N_2H_6^{++}$	20,450
Hg(g)	7,590	HN_3(aq)	65,300
Hg_2^{++}	36,850	N_3^-	70,750
Hg_2O	−12,800	NOCl(g)	16,010
HgO(red)	−13,940	NOBr(g)	19,260
Hg_2Cl_2	−50,310	**Osmium**	
Hg_2Br_2	−42,700	Os(g)	ca 112,000
Hg_2I_2	−26,530	OsO_4(s)	−69,400
Hg_2CO_3	−111,200	$HOsO_5^-$	−107,000
Hg^{++}	39,415	**Oxygen**	
HgO	−13,940	O(g)	55,025
HgS	−8,800	O_3(g)	39,400
$Hg(CN)_4^{--}$	140,400	H_2O(l)	−56,690
HgI_4^{--}	−51,150	H_2O(g)	−54,636
$HgBr_4^{--}$	−88,400	OH^-	−37,585
$HgCl_4^{--}$	−107,850	H_2O_2(g)	−24,730
$HgCl_2$	−42,200	H_2O_2(l)	−28,230
$HgBr_2$	−38,800	H_2O_2(aq)	−31,470
HgI_2(red)	−24,000	HO_2^-	−15,610
Molybdenum		OH(aq)	−5,000
Mo(g)	144,571	HO_2(aq)	3,000

Substance	$\Delta F°$	Substance	$\Delta F°$
Oxygen (*Cont.*)		**Rhodium** (*Cont.*)	
O_2^-	13,000	$RhCl_2$	−31,400
H_2O_3	ca 0	$RhCl_3$	−46,000
Palladium		$RhCl_3^{---}$	−156,000
Pd(g)	ca 101,000	**Rubidium**	
Pd^{++}	38,300	Rb(g)	13,352
$Pd(OH)_2$	ca −70,500	Rb^+	−68,800
$PdCl_4^{--}$	ca −96,000	RbH	−7,300
Phosphorus		**Ruthenium**	
P(s, w)	1,800	Ru(g)	ca 107,000
P_4(g)	13,100	$RuCl_3$	−49,200
P_2(g)	19,500	RuO_2	−40,500
P(g)	26,000	**Scandium**	
H_3PO_4(aq)	−270,000	Sc^{+++}	ca −138,000
$H_2PO_4^-$	−267,100	**Selenium**	
HPO_4^{--}	−257,270	Se(g)	17,800
PO_4^{---}	−240,970	H_2Se(g)	15,300
H_3PO_3(aq)	−204,000	H_2Se(aq)	16,720
$H_2PO_3^-$	−201,550	HSe^-	22,120
HPO_3^{--}	−193,150	Se^-	35,760
H_3PO_2(aq)	−120,000	H_2SeO_3(aq)	−101,361
$H_2PO_2^-$	−117,300	$HSeO_3^-$	−97,850
PH_3(g)	2,880	SeO_3^{--}	−87,890
P_4H_2(s)	16,000	$HSeO_4^-$	−107,840
PCl_3(l)	−61,500	SeO_4^{--}	−105,120
PI_2(s)	−5,700	SeF_6(g)	−219,000
Platinum		$SeCl_2$(l)	−13,730
Pt(g)	127,500	**Silicon**	
$Pt(OH)_2$	−67,900	SiO_2(α quartz)	−190,400
Pt^{++}	ca 55,000	H_2SiO_3(s)	−247,900
$PtCl_4^{--}$	−91,600	SiO_3^{--}	ca −215,000
PtS	−17,250	SiF_4(g)	−351,000
PtS_2	−21,000	SiF_6^{--}	−502,500
Polonium		$SiCl_4$(l)	−134,100
Po^{++}	ca 30,000	SiH_4(g)	−3,300
PoO_2	ca −106,000	SiC	−27,200
PoO_3^{--}	ca −102,000	**Silver**	
Potassium		Ag(g)	58,700
K(g)	14,637	Ag^+	18,441
K^+	−67,430	Ag_2O	−2,590
KH	−5,300	AgCl	−26,220
KCl	−97,555	AgBr	−22,900
KBr	−90,450	AgI(ppt)	−15,810
Rhenium		AgCN	38,500
ReO_4^-	−202,800	$Ag(CN)_2^-$	72,050
Rhodium		$Ag(NH_3)_2^+$	−4,060
Rh_2O	−17,400	$Ag(S_2O_3)_2^{---}$	−248,000
RhO	−19,300	$Ag(SO_3)_2^{---}$	−226,000
Rh_2O_3	−60,500	Ag_2S	−9,500
RhCl	−12,600	$AgNO_3$	4,960

Substance	$\Delta F°$	Substance	$\Delta G°$
Silver (*Cont.*)		**Sulfur** (*Cont.*)	
$AgIO_3$	−24,080	$SO_2Cl_2(g)$	−73,600
Ag_2CO_3	−104,600	$S_2Cl_2(l)$	−5,900
Ag_2SO_4	−145,940	**Tantalum**	
Ag^{++}	63,150	Ta_2O_5	−447,200
AgO	2,600	**Tellurium**	
Ag_2O_3	10,500	$Te_2(g)$	12,300
Sodium		$Te(g)$	46,000
$Na(g)$	18,639	$H_2Te(g)$	31,000
Na^+	−62,590	$H_2Te(aq)$	32,000
NaH	−9,300	HTe^-	35,500
Na_2O_2	−105,000	Te^{--}	42,300
$NaOH(s)$	−90,475	Te_2^{--}	38,750
$NaCl$	−91,700	$TeO_2(s)$	−64,530
Na_2CO_3	−250,800	$TeOOH^+$	−62,480
Strontium		$H_2TeO_3(aq)$	−115,700
$Sr(g)$	30,700	TeO_3^{--}	−110,100
Sr^{++}	−133,200	H_6TeO_6	−241,100
$SrCO_3$	−271,900	$TeCl_4$	−57,400
SrO_2	−139,000	$TeCl_6^{--}$	−137,400
SrH_2	−32,800	**Thallium**	
Sulfur		$Tl(g)$	31,700
$S(g)$	56,600	Tl^+	−7,760
$S_2(g)$	17,500	$Tl(OH)$	−45,535
$S(monocl)$	18.3	$TlCl$	−44,190
$S(l)$	94	$TlBr$	−39,750
$S_6(g)$	8,800	TlI	−29.976
$S_8(g)$	5,700	Tl^{+++}	49,740
$SO_2(g)$	−71,735	$Tl(OH)_3$	−123,000
$H_2S(g)$	−7,870	**Thorium**	
$H_2S(aq)$	−6,520	ThO_2	−280,100
HS^-	2,950	Th^{+4}	ca −197,000
S^{--}	23,420	ThH_4	−61,500
S_2^{--}	23,100	**Tin**	
S_3^{--}	22,400	Sn^{++}	−6,275
S_4^{--}	20,700	$Sn(OH)_2$	−115,950
$H_2SO_3(aq)$	−128,535	$HSnO_2^-$	−92,450
HSO_3^-	−125,905	SnS	−21,250
SO_3^{--}	−116,400	Sn^{+4}	ca 650
SO_4^{--}	−176,100	$Sn(OH)_4$	−226,000
$S_2O_3^{--}$	−124,000	$Sn(OH)_6^{--}$	ca −306,000
H_2SO_2	$>-90,000$	$SnCl_4(l)$	−110,600
$S_2O_4^{--}$	−130,000	**Titanium**	
$HS_2O_4^-$	−133,300	$TiO_2(rutile)$	−205,300
$S_2O_6^{--}$	−248,000	$TiO_2(amorph)$	−201,400
$S_3O_6^{--}$	−247,000	TiO^{++}	−144,400
$S_4O_6^{--}$	−240,000	Ti_2O_3	−340,800
$S_5O_6^{--}$	−237,000	TiF_6^{--}	−508,700
$H_2S_2O_8$	−257,000	**Tungsten**	
$SF_6(g)$	−235,000	$W(g)$	191,500

Substance	$\Delta F°$	Substance	$\Delta F°$
Tungsten (*Cont.*)		**Yttrium**	
WO_2	−118,300	Y^{+++}	ca −145,000
W_2O_3	−293,000	**Zinc**	
WO_3	−171,400	Zn(g)	22,692
WO_4^{--}	−220,000	Zn^{++}	−35,176
Uranium		$Zn(OH)_2$	−132,640
UO_2^{++}	−226,800	ZnO_2^{--}	−93,030
Na_2UO_4	−475,000	$Zn(NH_3)_4^{++}$	−72,740
UO_2	−242,200	ZnS	−43,200
Vanadium		$ZnCO_3$	−174,780
V(g)	75,000	**Zirconium**	
V_2O_5	−406,000	ZrO_2	−245,400
V_2O_3	−311,000	ZrO^{++}	−198,100
V^{++}	ca −70,000	$ZrO(OH)_2$	−307,600

APPENDIX III

Summary of Equilibrium Constants

Reaction	K
Aluminum	
$Al(OH)_3 = Al^{+++} + 3OH^-$	1.9×10^{-33}
$Al^{+++} + H_2O = Al(OH)^{++} + H^+$	1.4×10^{-5}
$Al(OH)_3 = H^+ + H_2AlO_3^-$	4×10^{-13}
$AlF_6^{---} = Al^{+++} + 6F^-$	ca 2×10^{-24}
Antimony	
$HSbO_2 = H^+ + SbO_2^-$	ca 10^{-11}
$\frac{1}{2}Sb_2O_3 + \frac{1}{2}H_2O = SbO^+ + OH^-$	10^{-17}
$Sb_2S_3 + H_2O + 2H^+ = 2SbO^+ + 3H_2S$	10^{-30}
Arsenic	
$HAsO_2 = H^+ + AsO_2^-$	6×10^{-10}
$HAsO_2 = AsO^+ + OH^-$	5.0×10^{-15}
$H_3AsO_4 = H^+ + H_2AsO_4^-$	4.8×10^{-3}
$H_2AsO_4^- = H^+ + HAsO_4^{--}$	10^{-7}
$HAsO_4^{--} = H^+ + AsO_4^{---}$	10^{-13}
$As_2S_3 + 4H_2O = 3H_2S + 2HAsO_2$	2×10^{-23}
Barium	
$BaCO_3 = Ba^{++} + CO_3$	4.93×10^{-9}
$BaC_2O_4 \cdot 2H_2O = Ba^{++} + C_2O_4^{--} + 2H_2O$	1.1×10^{-7}
$BaC_2O_4 \cdot 3\frac{1}{2}H_2O = Ba^{++} + C_2O_4^{--} + 3\frac{1}{2}H_2O$	1.62×10^{-7}
$Ba(HSO_4)_2 = Ba^{++} + 2HSO_4^-$	ca 2.7
$BaMnO_4 = Ba^{++} + MnO_4^{--}$	2.5×10^{-10}
$BaSO_4 = Ba^{++} + SO_4^{--}$	9.9×10^{-11}
$BaCrO_4 = Ba^{++} + CrO_4^{--}$	2×10^{-10}
$BaF_2 = Ba^{++} + 2F^-$	1.7×10^{-6}
$Ba(OH)_2 \cdot 8H_2O = Ba^{++} + 2OH^- + 8H_2O$	5.0×10^{-3}
$Ba(BrO_3)_2 \cdot H_2O = Ba^{++} + 2BrO_3^- + H_2O$	5.5×10^{-6}
$Ba(IO_3)_2 \cdot H_2O = Ba^{++} + 2IO_3^- + H_2O$	1.25×10^{-9}
$Ba(NO_3)_2 = Ba^{++} + 2NO_3^-$	4.5×10^{-3}
$BaCl_2 \cdot 2H_2O = Ba^{++} + 2H_2O + 2Cl^-$	1.6
Beryllium	
$2Be^{++} + H_2O = Be_2O^{++} + 2H^+$	4×10^{-7}
$H_2BeO_2(I) = 2H^+ + BeO_2^{--}$	2.8×10^{-30}
$H_2BeO_2(II) = 2H^+ + BeO_2^{--}$	1.4×10^{-30}
$Be_2O(OH)_2 + H_2O = 2Be^{++} + 4OH^-$	1×10^{-40}
$H_2Be_2O_3(s) = 2H^+ + Be_2O_3^{--}$	7.3×10^{-30}
$Be_2O(OH)_2 = Be_2O^{++} + 2OH^-$	4×10^{-19}
Bismuth	
$BiO(OH)(s) = BiO^+ + OH^-$	ca 1×10^{-12}
$BiOCl = BiO^+ + Cl^-$	7×10^{-9}

Reaction	*K*
Bismuth (*Cont.*)	
$BiOCl + H_2O = Bi^{+++} + Cl^- + 2OH^-$	1.6×10^{-31}
$BiOCl + 2H^+ + 3Cl^- = H_2O + BiCl_4^-$	0.8
$Bi_2S_3 = 2Bi^{+++} + 3S^{--}$	1.6×10^{-72}
Boron	
$H_3BO_3 = H_2BO_3^- + H^+$	5.8×10^{-10}
$4H_3BO_3 = H^+ + HB_4O_7^- + 5H_2O$	9.7×10^{-8}
$B_4O_7^{--} + 5H_2O = 2H_3BO_3 + 2H_2BO_3^-$	ca 10^{-3}
$HB_4O_7^- = H^+ + B_4O_7^{--}$	ca 10^{-9}
$H_2B_4O_7 = H^+ + HB_4O_7^-$	ca 10^{-4}
H_3BO_3 + glycerine = H_3BO_3·glycerine	0.9
H_3BO_3·glycerine = $H^+ + A^-$	3×10^{-7}
Phenylboric acid	137×10^{-10}
o-Tolylboric acid	18.1×10^{-10}
Benzylboric acid	75.5×10^{-10}
β-Phenylethylboric acid	10.0×10^{-10}
n-Butylboric acid	1.82×10^{-10}
Bromine	
$Br_2(aq) + Br^- = Br_3^-$	17
$Br_2 + H_2O = HBrO + H^+ + Br^-$	5.8×10^{-9}
$HBrO = H^+ + BrO^-$	2.06×10^{-9}
Cadmium	
$Cd(OH)_2 = Cd^{++} + 2OH^-$	1.2×10^{-14}
$Cd(NH_3)_4^{++} = Cd^{++} + 4NH_3$	2.5×10^{-7}
$CdS = Cd^{++} + S^{--}$	1.4×10^{-28}
$Cd(S_2O_3)_4^{-6} = Cd^{++} + 4S_2O_3^{--}$	ca 4×10^{-8}
$Cd(CN)_4^{--} = Cd^{++} + 4CN^-$	1.4×10^{-17}
$CdCO_3 = Cd^{++} + CO_3^{--}$	2.5×10^{-14}
$CdI_4^{--} = Cd^{++} + 4I^-$	ca 5×10^{-7}
Calcium	
$Ca(OH)_2 = Ca^{++} + 2OH^-$	7.9×10^{-6}
$CaCO_3 = Ca^{++} + CO_3^{--}$	4.82×10^{-9}
$CaSO_4 \cdot 2H_2O = Ca^{++} + SO_4^{--} + 2H_2O$	2.4×10^{-5}
$Ca_3(PO_4)_2 = 3Ca^{++} + 2PO_4^{--}$	1×10^{-25}
$CaHPO_4 = Ca^{++} + HPO_4^{--}$	ca 5×10^{-6}
$CaC_2O_4 \cdot H_2O = Ca^{++} + C_2O_4^{--} + H_2O$	2.27×10^{-9}
$CaC_4H_4O_6 \cdot 2H_2O = Ca^{++} + C_4H_4O_6^{--} + 2H_2O$	7.7×10^{-7}
$Ca(IO_3)_2 \cdot 6H_2O = Ca^{++} + 2IO_3^- + 6H_2O$	1.93×10^{-6}
$CaF_2 = Ca^{++} + 2F^-$	3.9×10^{-11}
Carbon	
$H_2CO_3 = H^+ + HCO_3^-$	4.31×10^{-7}
$HCO_3^- = H^+ + CO_3^{--}$	4.70×10^{-11}
$HCO_2H = H^+ + HCO_2^-$	1.77×10^{-4}
$H_2C_2O_4 = H^+ + HC_2O_4^-$	5.9×10^{-2}
$HC_2O_4^- = H^+ + C_2O_4^{--}$	6.4×10^{-5}
$HCN = H^+ + CN^-$	4×10^{-10}
$HCNO = H^+ + CNO^-$	1.2×10^{-4}
$HCNS = H^+ + CNS^-$	ca 10^{-4}
$C_6H_5NH_3^+ = C_6H_5NH_2 + H^+$	2×10^{-5}
$CO(NH_2)_2 + H_2O = CO(NH_2)(NH_3)^+ + OH^-$	1.5×10^{-14}

Reaction	*K*
Cerium	
$Ce_2(C_2O_4)_3 \cdot 10H_2O = 2Ce^{+++} + 3C_2O_4^{--} + 10H_2O$	2.5×10^{-29}
$Ce_2(C_4H_4O_6) \cdot 9H_2O = 2Ce^{+++} + 3C_4H_4O_6^{--} + 9H_2O$	9.7×10^{-20}
Cesium	
$CsClO_4 = Cs^+ + ClO_4^-$	4.05×10^{-3}
Chlorine	
$HClO = H^+ + ClO^-$	5.6×10^{-8}
$2HClO = Cl_2O(g) + H_2O$	3.54×10^{-3}
$HClO_2 = H^+ + ClO_2^-$	10^{-2}
Chromium	
$Cr(OH)_3 + 2H^+ = Cr(OH)^{++} + 2H_2O$	1×10^{8}
$CrCl_2^+ = Cr^{+++} + 2Cl^-$	1.26×10^{-2}
$Cr(OH)_3 = Cr^{+++} + 3OH^-$	6.7×10^{-31}
$Cr(OH)_3 = H^+ + CrO_2^- + H_2O$	9×10^{-17}
$HCrO_4^- = H^+ + CrO_4^{--}$	3.2×10^{-7}
$Cr_2O_7^{--} + H_2O = 2HCrO_4^-$	2.3×10^{-2}
Cobalt	
$Co(OH)_2 = Co^{++} + 2OH^-$	2×10^{-16}
$Co(NH_3)_6^{++} = Co^{++} + 6NH_3(aq)$	1.25×10^{-5}
$CoS(\alpha) = Co^{++} + S^{--}$	7×10^{-23}
$CoS(\beta) = Co^{++} + S^{--}$	1.9×10^{-27}
$CoCO_3 = Co^{++} + CO_3^{--}$	1.0×10^{-12}
$Co(OH)_3 = Co^{+++} + 3OH^-$	2.5×10^{-43}
$Co(NH_3)_6^{+++} = Co^{+++} + 6NH_3(aq)$	2.2×10^{-34}
$Co(NH_3)_5 \cdot H_2O^{+++} = Co^{+++} + 5NH_3(aq) + H_2O$	1.6×10^{-35}
$NaK_2Co(NO_2)_6 \cdot H_2O = Na^+ + 2K^+ + Co(NO_2)_6^{---}$	ca 2.2×10^{-11}
Copper	
$Cu + Cu^{++} = 2Cu^+$	1.0×10^{-6}
$\frac{1}{2}Cu_2O + \frac{1}{2}H_2O = Cu^+ + OH^-$	1.2×10^{-15}
$CuCl = Cu^+ + Cl^-$	1.85×10^{-7}
$CuBr = Cu^+ + Br^-$	5.3×10^{-9}
$CuI = Cu^+ + I^-$	1.1×10^{-12}
$CuCl + Cl^- = CuCl_2^-$	6.5×10^{-2}
$CuCl_2^- = Cu^+ + 2Cl^-$	2.9×10^{-6}
$CuBr + Br^- = CuBr_2^-$	4.6×10^{-3}
$CuI + I^- = CuI_2^-$	7.8×10^{-4}
$CuBr_2^- = Cu^+ + 2Br^-$	1.2×10^{-6}
$CuI_2^- = Cu^+ + 2I^-$	1.4×10^{-9}
$Cu(CN)_2^- = Cu^+ + 2CN^-$	1×10^{-16}
$CuCNS = Cu^+ + CNS^-$	4×10^{-14}
$Cu_2S = 2Cu^+ + S^{--}$	2.5×10^{-50}
$Cu(NH_2)_2^+ = Cu(NH_3)^+ + NH_3$	1.16×10^{-5}
$Cu(NH_3)_2^+ = Cu^+ + 2NH_3$	1.35×10^{-11}
$Cu(OH)_2 = Cu^{++} + 2OH^-$	5.6×10^{-20}
$H_2CuO_2 + 2OH^- = CuO_2^{--} + 2H_2O$	1.2×10^{-3}
$CuO + OH^- = HCuO_2^-$	1.03×10^{-5}
$CuO + 2OH^- = CuO_2^{--} + H_2O$	8.1×10^{-5}
$HCuO_2^- = H^+ + CuO_2^{--}$	7.9×10^{-14}
$CuS = Cu^{++} + S^{--}$	4×10^{-38}
$CuCO_3 = Cu^{++} + CO_3^{--}$	1.37×10^{-10}

Reaction	*K*
Copper (*Cont.*)	
$Cu(IO_3)_2 = Cu^{++} + 2IO_3^-$	1.3×10^{-7}
$Cu(NH_3)_5^{++} = Cu(NH_3)_4^{++} + NH_3$	2.8
$Cu(NH_3)_4^{++} = Cu^{++} + 4NH_3$	4.56×10^{-14}
Fluorine	
$HF(aq) = H^+ + F^-$	7.2×10^{-4}
$F^- + HF = HF_2^-$	5.5
Gallium	
$Ga(OH)^{++} = Ga^{+++} + OH^-$	4×10^{-12}
$Ga(OH)_2^+ = Ga(OH)^{++} + OH^-$	1.6×10^{-11}
$HGaO_3^{--} = GaO_3^{---} + H^+$	2×10^{-12}
$H_2GaO_3^- = HGaO_3^{--} + H^+$	4.8×10^{-11}
$Ga(OH)_3 = Ga^{+++} + 3OH^-$	ca 5×10^{-37}
$H_3GaO_3 = H_2GaO_3^- + H^+$	ca 1×10^{-15}
Germanium	
$H_2GeO_3(aq) = H^+ + HGeO_3^-$	2.6×10^{-9}
$HGeO_3^- = H^+ + GeO_3^{--}$	1.9×10^{-13}
$GeO_2(s) + H_2O = H^+ + HGeO_3^-$	1.1×10^{-10}
Gold	
$\frac{1}{2}Au_2O_3 + \frac{3}{2}H_2O = Au^{+++} + 3OH^-$	8.5×10^{-46}
$AuCl_4^- = Au^{+++} + 4Cl^-$	5×10^{-22}
$3Au^+ = Au^{+++} + 2Au$	ca 1×10^{-13}
$Au(CN)_2^- = Au^+ + 2CN^-$	ca 5×10^{-39}
$Au(CNS)_4^- = Au(CNS)_2^- + (CNS)_2$	4.9×10^{-5}
$3Au(CNS)_2^- = 2Au + Au(CNS)_4^- + 2CNS^-$	33
$Au(CNS)_4^- = Au^{+++} + 4CNS^-$	3×10^{-38}
Hafnium	
$HfO(OH)_2 = HfO^{++} + 2OH^-$	ca 10^{-25}
Indium	
$In^{+++} + H_2O = In(OH)^{++} + H^+$	2×10^{-4}
Iodine	
$I_2(aq) + I^- = I_3^-$	1.4×10^{-3}
$H_5IO_6 = H^+ + H_4IO_6^-$	2.3×10^{-2}
$H_4IO_6^- = H^+ + H_3IO_6^{--}$	ca 1×10^{-6}
$ICl_2^- = ICl(aq) + Cl^-$	6×10^{-3}
$2IBr(aq) = I_2(aq) + Br_2(aq)$	1.2×10^{-5}
$IBr_2^- = IBr(aq) + Br^-$	2.7×10^{-3}
$2ICl(aq) = I_2(aq) + Cl_2(aq)$	1.6×10^{-10}
$HIO = H^+ + IO^-$	ca 1×10^{-11}
Iridium	
$IrCl_6^{---} = Ir^{+++} + 6Cl^-$	ca 10^{-14}
$\frac{1}{2}Ir_2O_3 + \frac{3}{2}H_2O = Ir^{+++} + 3OH^-$	ca 10^{-45}
Iron	
$Fe(OH)_2 = Fe^{++} + 2OH^-$	1.65×10^{-15}
$FeCO_3 = Fe^{++} \times CO_3^{--}$	2.11×10^{-11}
$FeS = Fe^{++} + S^{--}$	1×10^{-19}
$Fe(CN)_6^{-4} = Fe^{++} + 6CN^-$	ca 10^{-37}
$Fe(OH)_3 = Fe^{+++} + 3OH^-$	4×10^{-38}
$Fe^{+++} + H_2O = Fe(OH)^{++} + H^+$	6.0×10^{-3}
$Fe^{+++} + Cl^- = FeCl^{++}$	20^{-4}

Reaction	*K*
Iron (*Cont.*)	
$Fe(C_2O_4)_3^{---} = Fe^{+++} + 3C_2O_4^{--}$	ca 10^{-10}
$2Fe^{+++} + Fe = 3Fe^{++}$	1×10^{41}
$Fe(CNS)_3 = Fe^{+++} + 3CNS^-$	2.6×10^{-6}
$Fe(CNS)_6^{---} = Fe(CNS)_3 + 3CNS^-$	3.1×10^{-4}
$Fe_2S_3 = 2Fe^{+++} + 3S^{--}$	10^{-88}
$Fe(CN)_6^{---} = Fe^{+++} + 6CN^-$	ca 10^{-44}
Lanthanum	
$La(OH)_3 = La^{+++} + 3OH^-$	ca 10^{-20}
Lead	
$Pb(OH)_2 = Pb^{++} + 2OH^-$	2.8×10^{-16}
$PbO(r) + H_2O = Pb^{++} + 2OH^-$	5.5×10^{-16}
$Pb(OH)_2 = H^+ + HPbO_2^-$	2.1×10^{-16}
$PbO(y) + OH^- = HPbO_2^-$	5.31×10^{-2}
$PbO(r) + OH^- = HPbO_2^-$	4.03×10^{-2}
$PbF_2 = Pb^{++} + 2F^-$	3.7×10^{-8}
$PbCl_2 = Pb^{++} + 2Cl^-$	1.7×10^{-5}
$PbBr_2 = Pb^{++} + 2Br^-$	6.3×10^{-6}
$PbI_2 = Pb^{++} + 2I^-$	8.7×10^{-9}
$PbCl^+ = Pb^{++} + Cl^-$	7.75×10^{-2}
$PbBr^+ = Pb^{++} + Br^-$	7.1×10^{-2}
$PbI^+ = Pb^{++} + I^-$	3.45×10^{-2}
$PbCO_3 = Pb^{++} + CO_3^{--}$	1.5×10^{-13}
$PbS = Pb^{++} + S^{--}$	1.0×10^{-29}
$PbCrO_4 = Pb^{++} + CrO_4^{--}$	1.8×10^{-14}
$Pb(IO_3)_2 = Pb^{++} + 2IO_3^-$	3.2×10^{-13}
$PbSO_4 = Pb^{++} + SO_4^{--}$	1.8×10^{-8}
$PbHPO_4 = Pb^{++} + HPO_4^{--}$	4×10^{-12}
$Pb_3(PO_4)_2 = 3Pb^{++} + 2PO_4^{---}$	3×10^{-44}
$PbO_2 + 2H_2O = Pb^{++} + 4OH^-$	10^{-64}
$Pb(BrO_3)_2 = Pb^{++} + 2BrO_3^-$	2.0×10^{-2}
$Pb_2PbO_4 = 2Pb^{++} + PbO_4^{-4}$	5.3×10^{-51}
Lithium	
$Li_2CO_3 = 2Li^+ + CO_3^{--}$	3.96×10^{-3}
$LiF = Li^+ + F^-$	5.2×10^{-3}
Lutecium	
$Lu(OH) = Lu^{+++} + 3OH^-$	ca 10^{-26}
Magnesium	
$Mg(OH)_2 = Mg^{++} + 2OH^-$	5.5×10^{-12}
$MgCO_3 \cdot 3H_2O = Mg^{++} + CO_3^{--} + 3H_2O$	ca 1×10^{-5}
$Mg(NH_4)PO_4 = Mg^{++} + NH_4^+ + PO_4^{---}$	2.5×10^{-13}
$MgF_2 = Mg^{++} + 2F^-$	6.4×10^{-9}
$MgC_2O_4 = Mg^{++} + C_2O_4^{--}$	8.6×10^{-5}
Manganese	
$Mn(OH)_2 = Mn^{++} + 2OH^-$	7.1×10^{-15}
$MnCO_3 = Mn^{++} + CO_3^{--}$	8.8×10^{-11}
$MnS = Mn^{++} + S^{--}$	5.6×10^{-16}
Mercury	
$Hg_2O + H_2O = Hg_2^{++} + 2OH^-$	1.6×10^{-23}

Reaction	*K*
Mercury (*Cont.*)	
$Hg_2Cl_2 = Hg_2^{++} + 2Cl^-$	1.1×10^{-18}
$Hg_2Br_2 = Hg_2^{++} + 2Br^-$	5.2×10^{-23}
$Hg_2I_2 = Hg_2^{++} + 2I^-$	4.5×10^{-29}
$Hg_2CO_3 = Hg_2^{++} + CO_3^{--}$	9×10^{-17}
$Hg_2SO_4 = Hg_2^{++} + SO_4^{--}$	6.2×10^{-7}
$Hg_2S = Hg_2^{++} + S^{--}$	1×10^{-45}
$Hg_2(CN)_2 = Hg_2^{++} + 2CN^-$	5×10^{-40}
$Hg_2(CNS)_2 = Hg_2^{++} + 2CNS^-$	3×10^{-20}
$Hg_2(IO_3)_2 = Hg_2^{++} + 2IO_3^-$	1.3×10^{-18}
$Hg_2(CH_3CO_2)_2 = Hg_2^{++} + 2CH_3CO_2^-$	2×10^{-15}
$Hg_2C_2O_4 = Hg_2^{++} + C_2O_4^{--}$	1×10^{-13}
$Hg_2C_4H_4O_6 = Hg_2^{++} + C_4H_4O_6^{--}$	1×10^{-10}
$Hg_2CrO_4 = Hg_2^{++} + CrO_4^{--}$	2×10^{-9}
$Hg + Hg^{++} = Hg_2^{++}$	81
$HgO + OH^- = HHgO_2^-$	3.15×10^{-5}
$HgO + H_2O = Hg^{++} + 2OH^-$	1.7×10^{-26}
$HgS = Hg^{++} + S^{--}$	3×10^{-53}
$HgCl_4^{--} = Hg^{++} + 4Cl^-$	1.1×10^{-16}
$HgBr_4^{--} = Hg^{++} + 4Br^-$	2.3×10^{-22}
$HgI_4^{--} = Hg^{++} + 4I^-$	5.3×10^{-31}
$Hg(CN)_4^{--} = Hg^{++} + 4CN^-$	4×10^{-42}
Nickel	
$Ni(OH)_2 = Ni^{++} + 2OH^-$	1.6×10^{-14}
$Ni(NH_3)_4^{++} = Ni^{++} + 4NH_3(aq)$	4.8×10^{-8}
$Ni(NH_3)_6^{++} = Ni^{++} + 6NH_3(aq)$	2.1×10^{-8}
$Ni(CN)_4^{--} = Ni^{++} + 4CN^-$	ca 1×10^{-22}
$NiCO_3 = Ni^{++} + CO_3^{--}$	1.36×10^{-7}
$NiS(\alpha) = Ni^{++} + S^{--}$	3×10^{-21}
$NiS(\beta) = Ni^{++} + S^{--}$	1×10^{-26}
$NiS(\gamma) = Ni^{++} + S^{--}$	2×10^{-28}
Nitrogen	
$HNO_2 = H^+ + NO_2^-$	4.5×10^{-4}
$2NO_2 = N_2O_4$	6.5
$NH_2OH(aq) + H_2O = NH_3OH^+ + OH^-$	6.6×10^{-9}
$NH_4OH = NH_4^+ + OH^-$	1.81×10^{-5}
$N_2H_4 + H_2O = N_2H_5^+ + OH^-$	8.5×10^{-7}
$N_2H_5^+ + H_2O = N_2H_6^{++} + OH^-$	8.9×10^{-16}
$HN_3 = H^+ + N_3^-$	ca 1×10^{-4}
$H_2N_2O_2 = 2H^+ + N_2O_2^{--}$	ca 1×10^{-17}
Osmium	
$H_2OsO_5 = H^+ + HOsO_5^-$	8×10^{-13}
Oxygen	
$H_2O = H^+ + OH^-$	1.008×10^{-14}
$OH^- = O^{--} + H^+$	$< 10^{-36}$
$O^{--} + H_2O = 2OH^-$	$> 10^{22}$
$H_2O_2 = H^+ + HO_2^-$	2.4×10^{-12}
Palladium	
$Pd(OH)_2 = Pd^{++} + 2OH^-$	ca 1×10^{-24}
$PdCl_4^{--} = Pd^{++} + 4Cl^-$	ca 3×10^{-7}

Reaction	K
Phosphorus	
$H_3PO_4 = H^+ + H_2PO_4^-$	7.5×10^{-3}
$H_2PO_4^- = H^+ + HPO_4^{--}$	6.2×10^{-8}
$HPO_4^{--} = H^+ + PO_4^{---}$	10^{-12}
$H_3PO_3 = H^+ + H_2PO_3^-$	1.6×10^{-2}
$H_2PO_3^- = H^+ + HPO_3^{--}$	7×10^{-7}
$H_3PO_2 = H^+ + H_2PO_2^-$	1×10^{-2}
$PH_4^+ = PH_3(g) + H^+$	ca 1
Platinum	
$Pt(OH)_2 = Pt^{++} + 2OH^-$	ca 1×10^{-35}
$PtCl_4^{--} = Pt^{++} + 4Cl^-$	ca 1×10^{-16}
$PtBr_4^{--} = Pt^{++} + 4Br^-$	ca 1×10^{-18}
$PtS = Pt^{++} + S^{--}$	ca 1×10^{-68}
Potassium	
$KClO_4 = K^+ + ClO_4^-$	1.07×10^{-2}
$KBrO_3 = K^+ + BrO_3^-$	5.7×10^{-2}
$KIO_3 = K^+ + IO_3^-$	5.0×10^{-2}
$K_2PtCl_6 = 2K^+ + PtCl_6^{--}$	1.1×10^{-5}
$K_2PdCl_6 = 2K^+ + PdCl_6^{--}$	6.0×10^{-6}
Radium	
$RaSO_4 = Ra^{++} + SO_4^{--}$	4.25×10^{-11}
Rubidium	
$RbClO_4 = Rb^+ + ClO_4^-$	2.5×10^{-3}
Scandium	
$Sc(OH)_3 = Sc^{+++} + 3OH^-$	ca 10^{-28}
Selenium	
$H_2Se = H^+ + HSe^-$	1.7×10^{-4}
$HSe^- = H^+ + Se^{--}$	ca 1×10^{-10}
$HSeO_4^- = H^+ + SeO_4^{--}$	ca 1×10^{-2}
Silicon	
$H_2SiO_3 = H^+ + HSiO_3^-$	1×10^{-10}
$HSiO_3^- = H^+ + SiO_3^{--}$	1×10^{-12}
$SiF_6^{--} + 2H_2O = SiO_2 + 4H^+ + 6F^-$	2×10^{-27}
$SiF_6^{--} = SiF_4(g) + 2F^-$	2×10^{-15}
Silver	
$\frac{1}{2}Ag_2O + \frac{1}{2}H_2O = Ag^+ + OH^-$	2.0×10^{-8}
$AgCl = Ag^+ + Cl^-$	1.7×10^{-10}
$AgBr = Ag^+ + Br^-$	3.3×10^{-13}
$AgI = Ag^+ + I^-$	8.5×10^{-17}
$AgCN = Ag^+ + CN^-$	7.0×10^{-15}
$Ag(CN)_2^- = Ag^+ + 2CN^-$	3.8×10^{-19}
$AgCNS = Ag^+ + CNS^-$	1.0×10^{-12}
$Ag(NH_3)_2^+ = Ag^+ + 2NH_3(aq)$	6.0×10^{-8}
$Ag(S_2O_3)_2^{---} = Ag^+ + 2S_2O_3^{--}$	4.2×10^{-14}
$Ag(SO_3)_2^{---} = Ag^+ + 2SO_3^{--}$	3.0×10^{-9}
$Ag_2S = 2Ag^+ + S^{---}$	1.0×10^{-51}
$AgNO_2 = Ag^+ + NO_2^-$	2.4×10^{-4}
$AgBrO_3 = Ag^+ + BrO_3^-$	5.20×10^{-5}
$AgIO_3 = Ag^+ + IO_3^-$	5.3×10^{-8}

Reaction	*K*
Silver (*Cont.*)	
$Ag_2CO_3 = 2Ag^+ + CO_3^{--}$	8.2×10^{-12}
$Ag_2C_2O_4 = 2Ag^+ + C_2O_4^{--}$	1.1×10^{-11}
$AgCNO = Ag^+ + CNO^-$	2.3×10^{-7}
$Ag_2CrO_4 = 2Ag^+ + CrO_4^{--}$	1.1×10^{-12}
$Ag_4Fe(CN)_6 = 4Ag^+ + Fe(CN)_6^{-4}$	1.55×10^{-41}
$Ag_2SO_4 = 2Ag^+ + SO_4^{--}$	1.18×10^{-5}
$Ag_2MnO_4 = 2Ag^+ + MnO_4^{--}$	3.1×10^{-11}
$AgWO_4 = 2Ag^+ + WO_4^{--}$	5.2×10^{-10}
$AgC_2H_3O_2 = Ag^+ + C_2H_3O_2^-$	1.9×10^{-3}
Sodium	
$NaF = Na^+ + F^-$	0.36
$NaHCO_3 = Na^+ + HCO_3^-$	0.62
$Na_2SO_4 = 2Na^+ + SO_4^{--}$	0.226
Strontium	
$Sr(OH)_2 \cdot 8H_2O = Sr^{++} + 2OH^- + 8H_2O$	3.2×10^{-4}
$Sr(HCO_3)_2 = Sr^{++} + 2HCO_3^-$	1.83×10^{-6}
$SrCrO_4 = Sr^{++} + CrO_4^{--}$	3.6×10^{-5}
$SrF_2 = Sr^{++} + 2F^-$	3×10^{-9}
$SrCO_3 = Sr^{++} + CO_3^{--}$	9.42×10^{-10}
$SrSO_4(ppt) = Sr^{++} + SO_4^{--}$	2.8×10^{-7}
$SrC_2O_4 \cdot H_2O = Sr^{++} + C_2O_4^{--} + H_2O$	5.61×10^{-8}
Sulfur	
$H_2S = H^+ + HS^-$	1.15×10^{-7}
$HS^- = H^+ + S^{--}$	1.0×10^{-15}
$H_2SO_3 = H^+ + HSO_3^-$	1.2×10^{-2}
$HSO_3^- = H^+ + SO_3^{--}$	1×10^{-7}
$HSO_4^- = H^+ + SO_4^{--}$	1.2×10^{-2}
$H_2S_2O_4 = H^+ + HS_2O_4^-$	0.45
$HS_2O_4^- = H^+ + S_2O_4^{--}$	3.5×10^{-3}
Tellurium	
$H_2Te = H^+ + HTe^-$	2.3×10^{-3}
$HTe^- = H^+ + Te^{--}$	ca 1×10^{-5}
$TeO_2 + H^+ = TeO_2H^+$	8.9×10^{-3}
$HTeO_3^- = TeO_3^{--} + H^+$	1×10^{-8}
$H_2TeO_3 = H^+ + HTeO_3^-$	2×10^{-3}
$TeO(OH)_2(aq) = TeOOH^+ + OH^-$	1×10^{-11}
Thallium	
$Tl(OH)_3 = Tl^{+++} + 3OH^-$	1.5×10^{-44}
$Tl(OH) = Tl^+ + OH^-$	7.2×10^{-1}
$TlCl = Tl^+ + Cl^-$	1.9×10^{-4}
$TlBr = Tl^+ + Br^-$	3.6×10^{-6}
$TlI = Tl^+ + I^-$	5.8×10^{-8}
$TlIO_3 = Tl^+ + IO_3^-$	4.5×10^{-6}
$TlBrO_3 = Tl^+ + BrO_3^-$	3.9×10^{-4}
$TlCNS = Tl^+ + CNS^-$	5.8×10^{-4}
$Tl_2S = 2Tl^+ + S^{--}$	1.2×10^{-24}
Thorium	
$Th(OH)_4 = Th^{+4} + 4OH^-$	ca 1×10^{-50}

Reaction	K
Tin	
$Sn(OH)_2 = Sn^{++} + 2OH^-$	5×10^{-26}
$H_2SnO_2 = H^+ + HSnO_2^-$	6×10^{-18}
$SnS = Sn^{++} + S^{--}$	8×10^{-29}
$Sn(OH)_4 = Sn^{+4} + 4OH^-$	ca 1×10^{-56}
$Sn(OH)_4 + 2OH^- = Sn(OH)_6^{--}$	2.1×10^{-4}
Titanium	
$TiO(OH)_2 = TiO^{++} + 2OH^-$	ca 1×10^{-30}
$\frac{1}{2}Ti_2O_3 + \frac{3}{2}H_2O = Ti^{+++} + 3OH^-$	ca 1×10^{-40}
Uranium	
$UO_2(OH)_2 = UO_2^{++} + 2OH^-$	2×10^{-15}
Vanadium	
$H_2V_6O_{17}^{--} = HV_6O_{17}^{---} + H^+$	1.1×10^{-2}
$HV_6O_{17}^{---} = V_6O_{17}^{-4} + H^+$	ca 1×10^{-5}
Ytterbium	
$Yb_2(C_2O_4)_3 \cdot 10H_2O = 2Yb^{+++} + 3C_2O_4^{--} + 10H_2O$	4.4×10^{-25}
Yttrium	
$Y(OH)_3 = Y^{+++} + 3OH^-$	ca 1×10^{-24}
Zinc	
$Zn^{++} + H_2O = Zn(OH)^+ + H^+$	2.45×10^{-10}
$Zn(OH)_2(S) = Zn^{++} + 2OH^-$	4.5×10^{-17}
$Zn^{++} + 4OH^- = ZnO_2^{--} + 2H_2O$	2.8×10^{15}
$ZnCO_3 = Zn^{++} + CO_3^{--}$	6×10^{-11}
$ZnS = Zn^{++} + S^{--}$	4.5×10^{-24}
$Zn(C_2O_4)_3^{-4} = Zn^{++} + 3C_2O_6^{--}$	1×10^{-9}
$Zn(CN)_4^{--} = Zn^{++} + 4CN^-$	2×10^{-17}
$Zn(NH_3)_4^{++} = Zn^{++} + 4NH_3(aq)$	9.8×10^{-10}
Zirconium	
$H_2ZrO_3(s) + OH^- = HZrO_3^- + H_2O$	ca 1×10^{-4}
$ZrO(OH)_2(s) = ZrO^{++} + 2OH^-$	ca 1×10^{-26}

APPENDIX IV

The Activity of Strong Electrolytes

The activity of a salt which ionizes according to the equation

$$X = \nu_+ X^+ + \nu_- X^-$$

is defined as:

$$a = a_+^{\nu+} a_-^{\nu-}.$$

The geometrical mean of the positive and negative ion activities is denoted as $a_\pm$:

$$a_\pm = a^{1/\nu}$$

where $\nu = \nu_+ + \nu_-$.

Example

For barium chloride,

$$a = a_{\mathrm{Ba}^{++}} \times a^2_{\mathrm{Cl}^-} = a_\pm^3.$$

If the molality is very low,

$$a_+ = \nu_+ m$$

$$a_- = \nu_- m$$

$$a_\pm = \left[(\nu_+ m)^{\nu+} (\nu_- m)^{\nu-}\right]^{1/\nu} = m(\nu_+^{\nu+} \nu_-^{\nu-})^{1/\nu}.$$

Example

For aluminum sulfate,

$$a_\pm = m(2^2 + 3^3)^{1/5}.$$

If the mean molality is defined as

$$m_\pm = m(\nu_+^{\nu+} \nu_-^{\nu-})^{1/\nu}$$

it is then possible to define a mean activity coefficient γ. This coefficient may be considered the thermodynamic degree of dissociation, and becomes equal to unity at infinite dilution for all types of salts:

$$\gamma = \frac{a_\pm}{m_\pm}$$

This mean activity coefficient, which might have been written $\gamma_\pm$, becomes in terms of the activity coefficients of the individual ions:

$$\gamma = (\gamma_+^{\nu+}\gamma_-^{\nu-})^{1/\nu}.$$

The activity coefficients of a large number of salts at varying molalities have been summarized in the table at the end of this appendix, and a few examples of typical curves of γ against $m^{\frac{1}{2}}$ are given in Figure 3.

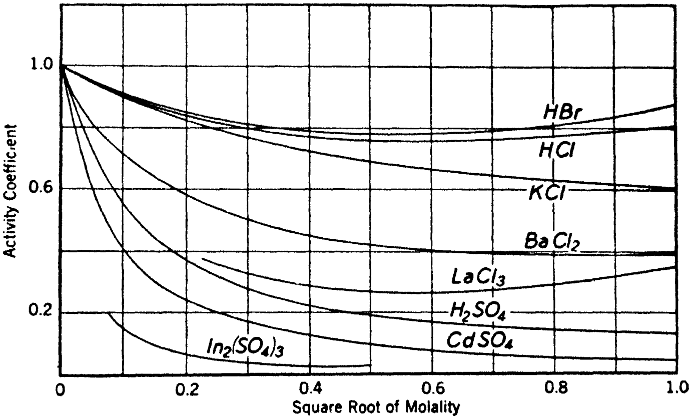

Fig. 3.—Plot of activity coefficients against square root of molality.

It was observed by G. N. Lewis as an empirical fact that, in a mixture of electrolytes, the activity coefficient of a salt is determined by the average ionic strength, μ, of the positive and negative ions, defined as

$$\mu = \frac{Z_+^2 m_+ + Z_-^2 m_-}{2} \quad \text{or} \quad \mu = \tfrac{1}{2}\Sigma\, m_i Z_i^2,$$

where Z is the charge on an ion.

Example

The ionic strength of $BaCl_2$ at a molality of m is

$$\mu = \frac{2^2m + 1^2(2m)}{2} = 3m.$$

The general principal may be stated: In dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength. The principal is to be looked upon as a limiting law, and large deviations occur at high concentrations.

The Debye and Hückel[1] theory has supplied the limiting laws for dilute solutions. Thus for a single ion

$$\log \gamma_i = -0.505\, Z_i^2 \mu^{\frac{1}{2}}$$

and for the mean activity of a salt,

$$\log \gamma = -0.505\, Z_+ Z_- \mu^{\frac{1}{2}}.$$

The data in Figure 3 have been replotted in Figure 4 in terms of $\frac{1}{Z_+Z_-} \log \gamma$ against $\mu^{\frac{1}{2}}$. It will be observed that for dilute solutions all the curves, except that for sulfuric acid, approach the limiting value (broken line). The behavior of the latter is to be accounted for by the weakness of the second dissociation step. If corrections are made for this, sulfuric acid also will fall upon one of the family of curves lying above the limiting line.

Randall and Vietti[2] have used the curves of Figure 4 in a graphical method of extrapolating potential measurements and equilibrium constants to zero ionic strength. As an example, we may discuss the application of the method by Bray and Hershey[3] to the ferrous-ferric electrode, that is to the reaction

$$Fe^{+++} + \tfrac{1}{2}H_2 = Fe^{++} + H^+.$$

Experimental e.m.f. values for the reaction must be obtained at fairly high hydrogen-ion concentration in order to prevent the hydrolysis of the ferric ion. For measurements in hydrochloric acid the potentials may be corrected to unit hydrogen ion activity from the known activity coefficients, and to equal concentrations of unhydrolyzed ferric and ferrous ions. This then gives the

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[1] Debye, P., and Hückel, E., Phys. Z., **24**, 185 (1923).

[2] Cf. Randall, M., and Vietti, W. A. V., J. Am. Chem. Soc., **50**, 1526 (1928). Unpublished calculations by Randall have also been available to the author.

[3] Bray, W. C., and Hershey, A. V., J. Am. Chem. Soc., **56**, 1889 (1934).

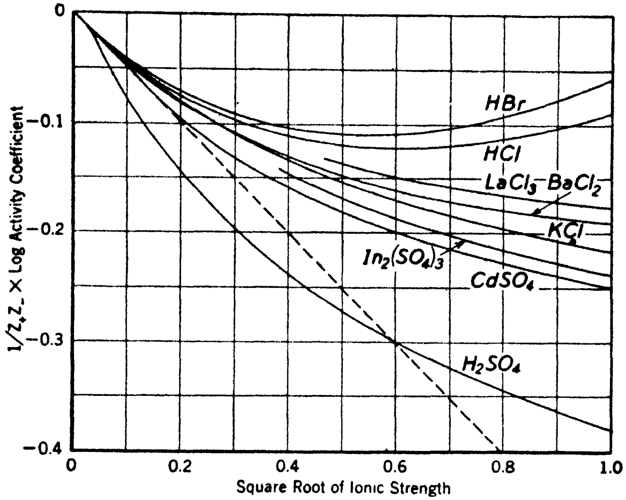

Fig. 4.—Plot of $\frac{\log \gamma}{Z_+ Z_-}$ against $\mu^{\frac{1}{2}}$.

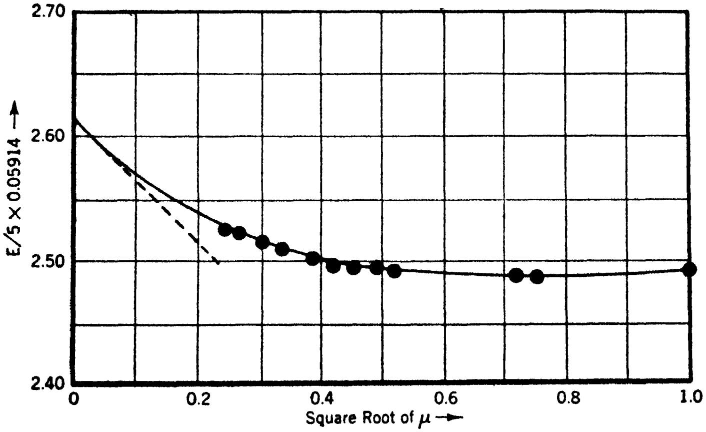

Fig. 5.—E/5 × 0.05914 for Fe^{++}-Fe^{+++} couple plotted against square root of ionic strength.

potential of Fe^{++}—Fe^{+++} couple in the hydrochloric acid solution. The E° value, however, refers to zero ionic strength and the extrapolation is a difficult problem.

The log γ-$\mu^{\frac{1}{2}}$ curve for a single ion approaches the limiting line whose slope is $0.505Z^2$. For the Fe^{++}—Fe^{+++} couple ΔZ^2 is 5 and the assumption is made that the curve for $E/5 \times 0.05914$ against $\mu^{\frac{1}{2}}$ will approach the limiting slope 0.505. A reproduction of the Bray and Hershey curve is given in Figure 5. The extrapolation to zero ionic strength is made by slipping the family of curves in Figure 4 over the experimental points until the best fit is secured. In this case it is a curve which lies just below that for HCl.

The problem of the extrapolation of this couple to zero ionic strength has been treated in a somewhat different manner by Schumb, Sherrill, and Sweetser.[4] These authors make use of an equation suggested by Guggenheim and Schindler[5]

$$\log \gamma = -0.505\ Z^2 \frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}}$$

which corresponds to about the average of the curves at low ionic strength. They calculate for each ionic strength a value

$$E' = E_{\text{observ.}} - 0.05914\ \Delta Z^2 \times 0.505 \frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}}.$$

E' is then plotted against μ and extrapolated to $\mu = 0$.

This method gives somewhat greater weight to the measurements at low ionic strength where the experimental errors are often quite large. The Randall method gives equal weight to all measurements throughout the concentration range but the assumption that the shape of the curve will always fit that of a curve for a single activity coefficient is open to some question.

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[4] Schumb, W. C., Sherrill, M. S., and Sweetser, S. B., J. Am. Chem. Soc., **59**, 2360 (1937).

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ACTIVITY COEFFICIENTS OF STRONG ELECTROLYTES

m	.001	.002	.005	.01	.02	.05	.1	.2	.5	1.0	2.0	3.0	4.0	Reference[a]
HCl	.966	.952	.928	.904	.875	.830	.796	.767	.758	0.809	1.01	1.32	1.76	(13)
HBr	.966	...	.929	.906	.879	.838	.805	.782	.790	0.871	1.17	1.67	...	(28), (50)
HNO_3	.965	.951	.927	.902	.871	.823	.785	.748	.715	0.720	0.783	0.876	0.982	(16), (1)
$HClO_4$	...	...	...	...	...	...	...	...	...	0.81	1.04	1.42	2.02	(14), (1)
HIO_3	.96	.94	.91	.86	.80	.69	.58	.46	.29	0.19	0.10	0.073	0.060	(15)
H_2SO_4	.830	.757	.639	.544	.453	.340	.265	.209	.154	0.130	0.124	0.141	0.171	(17)
NaOH	...	...	...	...	...	.82	...	.73	.69	0.68	0.70	0.77	0.89	(36)
KOH	...	...	.92	.90	.86	.82	.80	...	.73	0.76	0.89	1.08	1.35	(1), (28)
CsOH	...	...	...	.92	.88	.83	.80	.76	.74	0.78	...	...	...	(7), (1)
$Ba(OH)_2$	...	.853	.773	.712	.627	.526	.443	.370	...	...	...	...	...	(49)
$AgNO_3$	...	...	.92	.90	.86	.79	.72	.64	.51	0.40	0.28	...	...	(1), (2)
$Al(NO_3)_3$	...	...	...	...	...	...	.20	.16	.14	0.19	0.45	1.0	1.2	(44), (1)
$BaCl_2$	.88	...	.77	.72	...	.56	.49	.44	.39	0.39	0.44 (1.8m)	...	...	(27), (45)
$Ba(NO_3)_2$	.88	.84	.77	.71	.63	.52	.43	.34	...	...	...	...	...	(36), (1)
$Ba(IO_3)_2$	.83	.79	.71	.64	.55	...	...	...	...	...	...	...	...	(2)
$CaCl_2$	.89	.85	.785	.725	.66	.57	.515	.48	.52	0.71	...	...	...	(22)
$Ca(NO_3)_2$	.88	.84	.77	.71	.64	.54	.48	.42	.38	0.35	0.35	0.37	0.42	(19), (1)
$CdCl_2$	.76	.68	.57	.47	.38	.28	.21	.15	.09	0.06	...	...	...	(22)
CdI_2	.76	.65	.49	.38	.28	.17	.11	.068	.038	0.025	0.018	...	...	(25)
$CdSO_4$	.73	.64	.50	.40	.31	.21	.17	.11	.067	0.045	0.035	0.036	...	(3), (29)
CsF	.98	.97	.96	.95	.94	.91	.89	.87	.85	0.87	...	...	...	(8), (1)
CsCl	...	...	.92	.90	.86	.79	.75	.69	.60	0.54	0.49	0.48	0.47	(7), (1)
CsBr	...	...	.93	.90	.86	.79	.75	.69	.60	0.53	0.48	0.46	0.46	(4), (27), (1)
CsI	...	...	...	...	...	...	.75	.69	.60	0.53	0.47	0.43	...	(9)
$CsNO_3$	...	...	...	...	...	...	.73	.65	.52	0.42	...	...	...	(27)

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[a] Reference list will be found on pp. 326–327.

ACTIVITY COEFFICIENTS OF STRONG ELECTROLYTES (*Concluded*)

m	.001	.002	.005	.01	.02	.05	.1	.2	.5	1.0	2.0	3.0	4.0	Reference[a]
CsAc	...	...	...	...	...	...	.79	.77	.76	0.80	0.95	1.15	...	(27)
$CuCl_2$	.89	.85	.78	.72	.66	.58	.52	.47	.42	0.43	0.51	0.59	...	(10), (1)
$CuSO_4$	.74	...	.53	.41	.31	.21	.16	.11	.068	0.047	...	...	...	(11), (1), (29), (2)
$FeCl_2$	.89	.86	.80	.75	.70	.62	.58	.55	.59	0.67	...	...	...	(12)
$In_2(SO_4)_3$	...	...	...	.142	.092	.054	.035	.022	...	...	...	...	...	(30)
KF	...	.96	.95	.93	.92	.88	.85	.81	.74	0.71	0.70	...	...	(8), (1)
KCl	.965	.952	.927	.901	...	.815	.769	.719	.651	0.606	0.576	0.571	0.579	(24), (18), (20)
KBr	.965	.952	.927	.903	.872	.822	.777	.728	.665	0.625	0.602	0.603	0.622	(18)
KI	.965	.951	.927	.905	.88	.84	.80	.76	.71	0.68	0.69	0.72	0.75	(46), (1)
$K_4Fe(CN)_6$	...	...	...	...	...	.19	.14	.11	.067	...	...	...	...	(27)
$KClO_3$	.967	.955	.932	.907	.875	.813	.755	...	...	...	...	...	...	(21)
K_2CO_3	.89	.86	.81	.74	.68	.58	.50	.43	.36	0.33	0.33	0.39	0.49	(1)
$KClO_4$	.965	.951	.924	.895	.857	.788	...	....	...	...	...	...	...	(21)
K_2SO_4	.89	...	.78	.71	.64	.52	.43	.36	...	...	...	...	...	(2), (47), (1)
$LaCl_3$	...	...	...	...	...	.38	.32	.28	.27	0.36	...	...	...	(27)
$La(NO_3)_3$	...	...	...	.57	.49	.39	.33	.27	...	...	...	...	...	(2)
LiCl	.963	.948	.921	.89	.86	.82	.78	.75	.73	0.76	0.91	1.18	1.46	(8), (1)
LiBr	.966	.954	.932	.909	.882	.842	.810	.784	.783	0.848	1.06	1.35	...	(18), (9)
LiI	...	...	...	...	...	...	.81	.80	.81	0.89	1.19	1.70	...	(20)
$LiNO_3$	.966	.953	.930	.904	.878	.834	.798	.765	.743	0.76	0.84	0.97	...	(21), (9)
$LiClO_3$	.967	.955	.933	.911	.884	.842	.810	.782	.77	0.81	...	...	...	(21)
$LiClO_4$	.967	.956	.935	.915	.890	.853	.825	.805	.82	0.91	...	...	...	(21)
$MgCl_2$	...	...	...	...	...	...	.56	.53	.52	0.62	1.05	2.1	...	(1), (19)
$Mg(NO_3)_2$	.88	.84	.77	.71	.64	.55	.51	.46	.44	0.50	0.69	0.93	...	(1), (32)
$MgSO_4$	...	...	...	.40	.32	.22	.18	.13	.088	0.064	0.055	0.064	...	(2), (29)
$MnSO_4$	...	...	...	...	...	...	.25	.17	.11	0.073	0.058	0.062	0.079	(29)

[a] Reference list will be found on pp. 326–327.

m	.001	.002	.005	.01	.02	.05	.1	.2	.5	1.0	2.0	3.0	4.0	Reference[a]
$NiSO_4$	...	...	...	...	...	...	.18	.13	.075	0.051	0.041	...	...	(29)
NH_4Cl	.961	.944	.911	.88	.84	.79	.74	.69	.62	0.57	...	...	...	(33), (1)
NH_4Br	.964	.949	.901	.87	.83	.78	.73	.68	.62	0.57	...	...	...	(33), (1)
NH_4I	.962	.946	.917	.89	.86	.80	.76	.71	.65	0.60	...	...	...	(33), (1)
NH_4NO_3	.959	.942	.912	.88	.84	.78	.73	.66	.56	0.47	...	...	...	(33), (1)
$(NH_4)_2SO_4$	.874	.821	.726	.67	.59	.48	.40	.32	.22	0.16	...	...	...	(33), (1)
NaF	...	...	.93	.90	.87	.81	.75	.69	.62	...	...	...	...	(8), (1)
NaCl	.966	.953	.929	.904	.875	.823	.780	.730	.68	0.66	0.67	0.71	0.78	(34), (20), (18)
NaBr	.966	.955	.934	.914	.887	.844	.800	.740	.695	0.686	0.734	0.826	0.934	(18), (26)
NaI	.97	.96	.94	.91	.89	.86	.83	.81	.78	0.80	0.95	...	...	(8), (1), (9)
$NaNO_3$	.966	.953	.93	.90	.87	.82	.77	.70	.62	0.55	0.48	0.44	0.41	(35), (5)
Na_2SO_4	.887	.847	.778	.714	.641	.53	.45	.36	.27	0.20	...	...	...	(37), (38)
$NaClO_4$	.97	.95	.93	.90	.87	.82	.77	.72	.64	0.58	...	...	...	(21)
$PbCl_2$	.86	.80	.70	.61	.50	...	...	...	...	...	...	...	...	(22)
$Pb(NO_3)_2$	.88	.84	.76	.69	.60	.46	.37	.27	.17	0.11	...	...	...	(48)
RbCl	...	...	.93	.90	...	...	.76	.71	.63	0.58	0.54	0.54	0.54	(27), (1)
RbBr	...	...	...	...	...	...	.76	.70	.63	0.58	0.53	0.52	0.51	(27), (1)
RbI	...	...	...	...	...	...	.76	.70	.63	0.57	0.53	0.52	0.51	(21), (1)
$RbNO_3$	...	...	...	...	...	...	.73	.65	.53	0.43	0.32	0.25	0.21	(27)
RbAc	...	...	...	...	...	...	.73	.65	.52	0.42	...	...	...	(27)
TlCl	.96	.95	.93	.90	...	...	...	...	...	...	...	...	...	(2), (39)
$TlNO_3$	...	...	...	...	...	.77	.70	.60	...	...	...	...	...	(27)
$TlClO_4$	...	...	...	...	...	.79	.73	.65	.53	...	...	...	...	(27)
TlAc	...	...	...	...	...	.80	.74	.68	.59	0.51	0.44	0.40	0.38	(27)
$ZnCl_2$	.88	.84	.77	.71	.64	.56	.50	.45	.38	0.33	...	...	...	(22)
$ZnSO_4$	.70	.61	.48	.39	...	...	.15	.11	.065	0.045	0.036	0.04	...	(41), (42), (29)

[a] Reference list will be found on pp. 326–327.

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APPENDIX V

Entropy Values

In order to simplify the treatment, the experimental values for the entropies of the elements and compounds have not been given in the text. These values are summarized in the table below. The review by Kelley (reference 1) is such an excellent treatment that one can hardly do more, in general, than repeat his computations. However, a number of new entropies have been determined since the publication of the Kelley review, and these have been included. The values for the entropies of the aqueous ions, which have been the subject of an extensive series of investigations by the author and his co-workers, have been completely revised. In listing references, the original author has been given unless Kelley combined data from a number of sources.

Although many of the values given in the table have not been used directly in the free energy calculations of the text, a large number have been used indirectly as a basis for the estimation of the entropies of substances which have not been experimentally determined. For two solid substances of similar formulas and similar melting points, the difference in entropy arises very largely from the mass effect. The knowledge of the entropy of one substance then permits a close estimate of the value for that of the other by the expression,

$$S_{AX} - S_{BX} = \tfrac{3}{2} R \ln \frac{\text{at. wt.}_A}{\text{at. wt.}_B}.$$

ENTROPIES AT 298.15 K.

(Values in calories per degree per mole)

Substance	$S_{298.15}$	Reference[a]	Substance	$S_{298.15}$	Reference[a]
Aluminum			**Antimony**		
Al(s)	6.73	(2)	Sb(s)	10.5	(6)
Al(g)	39.31	(5)	Sb(g)	42.75	(5)
Al^{+++}	−76	(3)	Sb_2(g)	60.9	(1)
Al_2O_3	12.5	(1)	Sb_2O_3(s)	29.4	(6)

[a] Reference list will be found on pp. 334–336.

ENTROPIES AT 298.15 K. (Continued)

Substance	$S_{298.15}$	Reference[a]
Antimony (*Cont.*)		
Sb_2O_4	30.4	(6)
Sb_2O_5	29.9	(6)
$SbCl_3$(s)	44.8	(1)
Arsenic		
As(s)	8.4	(7)
As(g)	41.62	(5)
As_4(g)	68.7	(1)
As_2O_3	25.6	(7)
As_2O_5	25.2	(7)
$AsCl_3$(g)	78.2	(30)
Barium		
Ba(s)	15.1	(88)
Ba(g)	40.67	(5)
Ba^{++}	2.3	(3)
$Ba(BrO_3)_2 \cdot H_2O$	69	(40)
$BaCO_3$	26.8	(15)
$BaCl_2 \cdot 2H_2O$	48.58	(20)
$Ba(NO_3)_2$	51.1	(39)
BaO(s)	16.8	(10)
$BaSO_4$	31.5	(42)
BaF_2	23.03	(93)
Beryllium		
Be(s)	2.28	(1), (45)
Be(g)	32.53	(5)
Bismuth		
Bi(s)	13.6	(1)
Bi(g)	44.68	(5)
Bi_2(g)	65.4	(1)
Bi_2O_3	32.2	(6)
$BiCl_3$(s)	46	(1)
Boron		
B(s)	(1.5)	(88)
B(g)	36.66	(1)
Bromine		
Br_2(l)	36.8	(46)
Br_2(g)	58.63	(1)
Br(g)	41.81	(5)
Br^-	19.7	(3)
HBr	47.48	(48)
BrCl	57.1	(51)
BrO_3^-	38.5	(3)
Cadmium		
Cd(s)	12.3	(1)
Cd(g)	40.07	(5)
Cd^{++}	16.4	(3)
$CdBr_2$	34.4	(1)
Cadmium (*Cont.*)		
$CdCl_2$	31.5	(1), (53)
$CdCO_3$	25.2	(1)
CdO	13.1	(1)
$Cd(OH)_2$	21.2	(1)
CdS	15.0	
Calcium		
Ca(s)	9.9	(52), (1)
Ca(g)	37.00	(5)
Ca^{++}	11.4	(3)
$CaCO_3$(calcite)	22.2	(15), (1)
$CaCO_3$(aragonite)	21.2	(15), (1)
$CaC_2O_4 \cdot H_2O$	37.3	(43)
CaF_2	16.4	(1)
CaH_2	9.9	(1)
CaO	9.5	(54)
$Ca(OH)_2$	18.2	(40)
$CaSO_4 \cdot 2H_2O$	46.4	(42)
$CaSO_4$	25.6	(1)
Carbon		
C(graphite)	1.36	(55)
C(diamond)	0.585	(58)
C(g)	37.77	(1)
C_2(g)	47.9	(1)
CCl_4(g)	74.3	(56)
CCl_4(l)	51.5	(56)
CH_4	44.5	(57)
C_2N_2	57.8	(60)
CO	47.32	(61)
CO_2	51.08	(17)
CO_3^{--}	−13.0	(3)
HCO_3^-	22.2	(3)
H_2CO_3(aq)	45.1	(3), (59)
CS_2(l)	36.1	(19)
COS	55.3	(18)
$C_2O_4^{--}$	9.6	(3)
HCN(g)	48.2	(62)
CN^-	25	(3)
Cerium		
Ce(s)	13.8	(4)
Ce(g)	48.1	(5)
CeO_2	(17.7)	(1)
Cesium		
Cs(s)	19.8	(1)
Cs(g)	41.95	(5)

[a] Reference list will be found on pp. 334–336.

ENTROPIES AT 298.15 K. (*Continued*)

Substance	$S_{298.15}$	Reference[a]
Cesium (*Cont.*)		
$CsAl(SO_4)_2 \cdot 12H_2O$	16.4	(40)
$CsClO_4$	41.9	(93)
Chlorine		
Cl_2	53.31	(63)
Cl(g)	39.47	(1)
HCl(g)	44.66	(49)
Cl^-	13.50	(3)
Cl_2O	67.9	(1)
ClO_2	58.5	(1)
ClO^-	10.0	(3)
ClO_2^-	24.1	(3)
ClO_3^-	39.4	(3)
ClO_4^-	43.6	(3)
Chromium		
Cr(s)	5.68	(1)
Cr(g)	41.64	(5)
Cr_2O_3	19.4	(1)
CrO_4^{--}	10.5	(3)
Cobalt		
CO(s)	6.8	(1)
Copper		
Cu(s)	7.97	(1)
Cu(g)	39.75	(5)
$Cu_2(g)$	58.9	(64)
Cu^{++}	−26.5	(3)
CuBr	22.8	(1)
CuCl	20.8	(1)
CuI	23.1	(1)
$CuCO_3$	17.7	(1)
Cu_2O	24.0	(1)
CuO	10.4	(1)
Cu_2S	28.9	(1)
CuS	15.9	(1)
$CuSO_4$	25.3	(1)
Fluorine		
$F_2(g)$	48.00	(1)
F(g)	37.93	(1)
HF	41.5	(1)
F^-	−2.3	(3)
F_2O	59	(88)
Gadolinium		
$Gd_2(SO_4)_3 \cdot 8H_2O$	155.7	(1)
Gallium		
Ga(s)	10.2	(1)
Ga(g)	40.03	(1)
Germanium		
Ge(s)	10.1	(1)
Gold		
Au(s)	11.4	(1)
Au(g)	43.13	(5)
Hafnium		
Hf(s)	13.1	(45)
Helium		
He(g)	30.13	(5)
Hydrogen		
H_2	31.23	(23)
D_2	34.62	(65)
H	27.40	(5)
H^+	0.00	(3)
$H_2O(g)$	45.13	(16)
$H_2O(l)$	16.75	(26), (16)
$D_2O(g)$	46.66	(27)
$D_2O(l)$	18.08	(27)
Indium		
In(s)	(14.5)	(66)
In(g)	41.51	(5)
Iodine		
$I_2(s)$	27.9	(67)
$I_2(g)$	62.29	(67)
I(g)	43.19	(5)
HI	49.40	(50)
I^-	25.3	(3)
IBr(g)	62.0	(51)
IBr(s)	33.2	(51)
ICl(g)	59.15	(51)
$ICl_3(s)$	27.3	(68)
IO_3^-	28.0	(3)
Iridium		
Ir(s)	8.7	(4)
Iron		
Fe(s)	6.5	(1)
Fe(g)	43.12	(1)
Fe^{++}	−25.9	(3)
Fe^{+++}	−63.3	(3)
$FeCO_3$(siderite)	22.2	(9)
$FeCl_2$	29.4	(1)
FeO	14.2	(1)
Fe_2O_3	21.5	(54)
Fe_3O_4	35.0	(54)
FeS	16.1	(1)
Lanthanum		
La(s)	13.7	(4)

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[a] Reference list will be found on pp. 334–336.

ENTROPIES AT 298.15 K. (*Continued*)

Substance	$S_{298.15}$	Reference[a]
Lead		
$Pb(s)$	15.50	(4)
$Pb(g)$	41.90	(5)
Pb^{++}	3.9	(3)
$PbCl_2$	32.6	(1)
$PbBr_2$	38.6	(46)
PbI_2	42.2	(69)
$PbCO_3$	31.3	(9)
PbO	16.9	(1)
PbO_2	18.3	(1)
Pb_3O_4	50.5	(1)
PbS	21.8	(1)
$PbSO_4$	35.2	(12)
$Pb_3(PO_4)_2$	84.45	(93)
Lithium		
$Li(s)$	6.70	(70)
$Li(g)$	33.15	(5)
$Li_2(g)$	47.01	(1)
Li^+	4.7	(3)
LiH	6.0	(71)
$LiOH$	12.8	(1)
Li_2SO_4	35.3	(1)
Li_2CO_3	21.60	(29)
Magnesium		
$Mg(s)$	7.76	(52)
$Mg(g)$	35.51	(5)
Mg^{++}	−31.6	(3)
$MgCO_3$	15.7	(9)
MgO	6.66	(16)
$Mg(OH)_2$	15.19	(16)
Manganese		
$Mn(s)$	7.3	(4)
$Mn(g)$	41.50	(5)
$MnCO_3$	20.5	(9)
MnO	14.4	(1)
MnO_2	13.9	(1)
Mn_3O_4	35.5	(1)
MnS	18.7	(1)
Mercury		
$Hg(l)$	18.5	(1)
$Hg(g)$	41.80	(5)
Hg^{++}	−6.5	(40)
Hg_2^{++}	17.7	(3)
Hg_2Cl_2	47.0	(1)
Hg_2Br_2	52.8	(74), (1)
$HgO(red)$	16.5	(1)
$HgO(yellow)$	17.5	(1)
Mercury (*Cont.*)		
HgS	19.8	(1)
Hg_2SO_4	47.9	(1)
Molybdenum		
$Mo(s)$	6.8	(72)
$Mo(g)$	43.47	(5)
MoS_2	15.1	(1)
Neon		
$Ne(g)$	34.96	(5)
Nickel		
$Ni(s)$	7.1	(75), (1)
$Ni(g)$	43.54	(1)
Nitrogen		
N_2	45.79	(22)
$N(g)$	36.62	(5)
N_2O	52.58	(77)
NO	50.34	(78), (79)
$NO_2(g)$	57.47	(76)
$N_2O_4(g)$	72.73	(76)
$N_2O_5(s)$	36.6	(1)
$N_2O_5(g)$	81.8	(1)
$NOBr(g)$	65.2	(80), (1)
$NOCl(g)$	60.5	(1)
$NH_3(g)$	45.91	(21)
NH_4^+	26.4	(3)
$NH_4OH(aq)$	42.8	(3), (59)
NH_4Cl	31.8	(1)
NO_2^-	29.9	(3)
NO_3^-	35.0	(3)
Osmium		
$Os(s)$	7.8	(4)
Oxygen		
O_2	49.03	(81)
$O(g)$	38.48	(1)
O_3	57.1	(1)
$OH(g)$	43.9	(82)
$OH^-(aq)$	−2.49	(3)
Palladium		
$Pd(s)$	8.9	(4)
Phosphorus		
$P(red)$	(7)	(88)
$P(yellow)$	15.1	(30)
$P(g)$	38.99	(5)
$P_2(g)$	52.0	(30)
$P_4(g)$	84.9	(30)
$PH_3(g)$	50.35	(24)
$PBr_3(g)$	83.4	(1)

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[a] Reference list will be found on pp. 334–336.

ENTROPIES AT 298.15 K. (*Continued*)

Substance	$S_{298.15}$	Reference[a]
Phosphorus (*Cont.*)		
$PCl_3(l)$	52.2	(1)
$PF_3(g)$	64.2	(30)
PH_4I	32.1	(1)
Platinum		
Pt(s)	10.0	(72), (1)
Potassium		
K(s)	15.2	(72), (1)
K(g)	38.30	(5)
$K_2(g)$	59.5	(1)
K^+	24.2	(3)
KCl	19.75	(87)
KBr	22.5	(2)
KI	24.1	(1)
$KClO_3$	34.2	(44)
$KClO_4$	36.1	(84)
$KBrO_3$	35.6	(83)
KIO_3	36.2	(83)
KNO_3	31.78	(87)
K_2SO_4	44.8	(1)
$KMnO_4$	41.04	(25)
Rhodium		
Rh	7.6	(4)
Rubidium		
Rb(s)	18.1	(88)
Rb(g)	40.64	(5)
Rb^+	28.7	(3)
$RbClO_4$	36.3	(28)
Ruthenium		
Ru(s)	6.9	(4)
Samarium		
$Sm_2(SO_4)_3 \cdot 8H_2O$	161.0	(1)
Selenium		
Se(s)	10.5	(9)
$SeF_6(g)$	75.2	(1)
Silicon		
Si(s)	4.5	(2)
Si(g)	40.13	(1)
SiC	3.90	(1)
$SiCl_4(g)$	79.2	(56)
$SiCl_4(l)$	57.4	(1)
$SiH_4(g)$	49.03	(1)
SiO_2(quartz)	10.1	(13)
SiO_2(cristobalite)	10.35	(13)
SiO_2(tridymite)	10.5	(13)

Substance	$S_{298.15}$	Reference[a]
Silicon (*Cont.*)		
SiO_2(glass)	11.2	(1)
Silver		
Ag(s)	10.2	(2)
Ag(g)	41.33	(5)
Ag_2O	29.09	(31)
Ag^+	17.54	(3)
AgCl	22.97	(85)
AgBr	25.62	(85)
AgI	27.6	(1)
Ag_2CO_3	40.0	(14)
$AgIO_3$	36.0	(40)
Ag_2S	35.0	(1)
Ag_2SO_4	47.8	(41)
$AgNO_3$	33.68	(32)
$Ag(NH_3)_2^+$	57.8	(3)
Ag_2CrO_4	51.82	(33)
$AgClO_2$	32.16	(34)
Sodium		
Na(s)	12.2	(1)
Na(g)	36.72	(5)
$Na_2(g)$	54.9	(1)
Na^+	14.0	(3)
NaCl	17.3	(1)
NaBr	20.1	(73)
NaI	22.5	(73)
Na_2CO_3	32.5	(14)
$NaHCO_3$	24.4	(14)
NaOH	13.8	(86), (1)
$NaNO_3$	27.87	(87)
Na_2SO_4	35.73	(47)
$Na_2SO_4 \cdot 10H_2O$	142.2	(47)
Strontium		
Sr(s)	13.3	(88)
Sr(g)	39.33	(5)
SrO	13.0	(10)
$SrCO_3$	23.2	(15)
Sulfur		
S(r)	7.62	(35)
S(m)	7.78	(35)
S(g)	40.10	(1)
$S_2(g)$	54.41	(1)
$S_6(g)$	92.2	(1)
$S_8(g)$	109.2	(1)
S^{--}	−5.5	(40)
HS^-	14.9	(3)
$H_2S(g)$	49.15	(36), (37)

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[a] Reference list will be found on pp. 334–336.

ENTROPIES AT 298.15 K. (*Continued*)

Substance	$S_{298.15}$	Reference[a]
Sulfur (*Cont.*)		
$SF_6(g)$	69.6	(1)
$SO(g)$	53.1	(89)
$SO_2(g)$	59.3	(1)
SO_4^{--}	4.4	(3)
HSO_4^-	30.6	(3)
SO_3^{--}	3	(3)
HSO_3^-	32.6	(3)
Tantalum		
$Ta(s)$	9.4	(1)
Tellurium		
$Te(s)$	12.85	(8)
$Te_2(g)$	64.5	(1)
$TeF_6(g)$	80.8	(1)
Thallium		
$Tl(s)$	15.5	(52)
$Tl(g)$	43.23	(5)
Tl^+	30.5	(3)
$TlCl$	24.8	(1)
$TlBr$	26.8	(1)
TlI	29.9	(1)
$TlNO_3$	38.1	(38)
Thorium		
$Th(s)$	13.6	(4)
ThO_2	(19.6)	(1)
Tin		
Sn(white)	12.4	(2)
Sn(grey)	10.7	(2)
$Sn(g)$	40.24	(5)
Sn^{++}	−4.9	(3)
$SnCl_4(l)$	62.1	(56), (1)
Tin (*Cont.*)		
SnO	13.5	(1)
SnO_2	12.5	(1)
Titanium		
$Ti(s)$	6.6	(4)
$TiCl_4(l)$	60.4	(56), (1)
Tungsten		
$W(s)$	8.0	(1)
WO_3	(18.3)	(1)
Uranium		
$U(s)$	11.1	(4)
U_3O_8	(72.7)	(1)
Vanadium		
$V(s)$	7.0	(11)
V_2O_3	23.5	(11)
V_2O_4	24.5	(11)
V_2O_5	31.3	(11)
Zinc		
$Zn(s)$	9.95	(1)
$Zn(g)$	38.46	(5)
Zn^{++}	−25.7	(3)
ZnO	10.4	(1)
ZnS	13.8	(1)
$ZnSO_4$	30.6	(91), (1)
$ZnCO_3$	19.7	(9)
$ZnCl_2$	24.3	(90)
$ZnCl_2(NH_3)_4$	109.6	(90)
$ZnBr_2$	32.2	(92), (1)
Zirconium		
$Zr(s)$	9.5	(4)

[a] Reference list will be found on pp. 334–336.

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